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Development of Methods and Techniques for Final Treatment of Combined Municipal and Textile Wastewater Including Sludge Utilization and Disposal

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16. ABSTRACT

The investigations were carried out on laboratory scale, employing various mixtures of dyeing and municipal wastewaters. The processes studied were: coagulation, ozonization, chlorination, activated carbon, activated sludge, and anaerobic digestion.

The most widely used dye from each class of dyes was chosen for determining adsorption isotherms. The results showed that activated carbon is quite selective and cannot be used to treat some dye wastes. Activated carbon was found to be particularly efficient in final treatment of dyeing wastewaters. Activated sludge and anaerobic digestion, while effective in removing BOD constituents, were not effective in removing color. Many of the dyes were inhibitory to digestors.

Lime appeared to be the best coagulation agent. Feasibility of lime reclamation by recalcining the sludge and recycling the lime in the coagulation process was demonstrated.

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DEVELOPMENT OF METHODS AND TECHNIQUES FOR FINAL TREATMENT OF COMBINED MUNICIPAL AND TEXTILE WASTEWATER INCLUDING SLUDGE UTILIZATION AND DISPOSAL

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This study was concerned with evaluating various combinations of wastewater treatment processes for their effectiveness to treat a combination of domestic and textile wastes. Special emphasis was placed on color elimination. The investigations were carried out on laboratory scale, employing various mixtures of dyeing and municipal wastewaters.

Francis T. Mayo
Director, Municipal Environmental
Research Laboratory

ABSTRACT

The report contains the results of studies and technological investigations, which were aimed at the estimation of the usability of unit methods of wastewater treatment, and sludge processing for the treatment of textile wastewater, and towards choosing treatment technologies of these wastewaters.

In addition to the usability studies, the evaluation of identification methods of dyeing wastewater components was done. The investigations were carried out on laboratory scale. Technological studies included the following methods: coagulation, ozonization, chlorination, bromination, adsorption, activated sludge, anaerobic digestion of wastewater and sludge.

Based on the investigations, it can be stated that the dyeing wastewater can be effectively treated using aerobic and anaerobic processes of wastewater biological treatment. Wastewater cleaned biologically, particularly in aerobic processes, however, are characterized in general by high color. Physical and chemical methods remove color from dyeing wastewater, and give a satisfactory organic substances removal.

The work has been accomplished within the Polish American agreement Project PL-480, Grant PR5-532-2 by the Institute of Environmental Development, Environmental Pollution Abatement Centre at Katowice, Poland, for the U.S. Environmental Protection Agency.

The work was finished in October 1976.

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SECTION 1

INTRODUCTION

The textile industry has undergone a change in the type of cloth and fibers being used. There has been a switch from cotton, wool and silk to the use of synthetic fibers. With this change the type of dye, dispersing agents, fixers, etc. have changed considerably. Engineers in the wastewater treatment field need to know about the effects of these new substances on wastewater treatment systems. In that textile wastes result from a variety of technological processes and the use of many different raw materials, the wastes are very complex.

Although the selection of optimum processes of wastewater treatment should be accomplished individually for each site, much can be learned from a general approach to the problem. To gain an insight into the treatability of today's textile wastes, various combinations of wastewater treatment processes were investigated. Special emphasis was given to color removal.

The effectiveness of hydrolysis, chemical and biological oxidation, and adsorption were evaluated. The toxic effects of various dyes and complex textile wastes on anaerobic digestion were studied.

SECTION 2

CONCLUSIONS

The effective treatment of textile wastewater with the addition or without municipal wastewater is possible by use of physical and chemical treatment methods. Color removal is obtained by oxidation using ozone, chlorine or bromine. During the oxidation process considerable amount of the oxidant is consumed, which can be substantially decreased by the use of catalysts. Ultraviolet radiation was found to be a perfect catalyst for the oxidation reaction with chlorine.

The decomposition of dyes structure can also be obtained in the process of hydrolysis with lime. In this process a pH above 10 is required. The addition of lime causes only partial discoloration of wastewater in case of mixtures of dyes, because of the various effectiveness of the hydrolysis process in relation to individual dyes.

The biological methods of wastewater treatment show relatively low effectiveness of color removal from wastewater. Aerobic biochemical processes in general did not lead towards substantial structural changes of dyes. Changes of dyes structure due to aerobic biochemical processes were studied.

Initiation of dyes decomposition in anaerobic process allows for further decomposition in subsequent aerobic processes. More attention should be paid in the future to the two-stage biological treatment method, with anaerobic process as a first process and for instance, activated sludge as a second process.

SECTION 3

RECOMMENDATIONS

The investigations carried out were aimed at the working out of treatment methods for textile wastewater, especially dyeing wastewater occurring as a mixture of dye baths only or together with municipal wastewaters.

Based on these studies the following recommendations can be made:

- In case of the mixture of textile wastewater and the municipal in which textile wastewater is in prevailing amount, the chemical treatment method should be used. This method consists in the addition of CaO, and aluminum or ferric sulfate. Considering the high value of pH, the wastewater must be neutralized before it is discharged into the receiving water.

- In some cases the treatment of wastewater can be carried out by catalyzed chlorination process.

- The mixture of textile wastewater with a considerable portion of municipal wastewater can be effectively treated by the use of biological methods.

- To obtain effective removal of color from wastewater, the application of at least a two-stage process of biological treatment is recommended. The first stage should be an anaerobic process and the second one an aerobic process.

- If the textile wastewater contains heavy metals, the toxic effects can be eliminated by the addition of small doses of CaO to wastewater entering the primary settling tanks.

- Ozonization or adsorption process on activated carbon should be applied only if necessary as a final stage of wastewater treatment.

Before the ozonization, or carbon adsorption, the wastewater should be free of suspended solids.

SECTION 4

CHARACTERISTICS OF SUBSTRATES USED FOR THE INVESTIGATIONS

Typical dyes and solutions of dyeing wastewater and mixtures with municipal wastewater were the basic substrates.

Tap water solutions containing dye baths, and assistants were used for wastewater treatment by the coagulation method. The investigations were carried out for three different concentrations of the mixtures, i.e. for 0.1%, 0.5% and 3%. See Table 1. In addition, investigations were done for 0.1% solution of selected mixtures of dye baths, and assistants and municipal wastewater.

For treatment by ozonization, chlorination and bromination methods, the above mentioned solutions of dye baths and assistants of 0.1% and 0.5% (concentration) were used.

Treatment by ozonization was also carried out separately for 0.005% distilled water solutions of the following dyes:

- reactive dye - lunasol Rot 5B
- basic dye - special basic red BLN
- welan dye - welan brown
- sulfuric dye - sulfuric brown

For wastewater treatment by activated carbon and bentonite adsorption method, tap water solutions of individual dye baths as well as mixtures of these solutions were used. The investigations were carried out for the following concentrations of dye baths:

10% solution of dye bath - for metallized dyes
5% solution of dye bath - for direct, sulfur, dispersed and basic dyes
1% solution of dye bath - for reactive dyes
0.5% solution of dye bath - for chrome dyes
1% solution of mixture of all tested dye baths.

The composition of the individual solutions of dye baths are given in Table 2. Additional investigations were done on wastewater treatment by activated carbon adsorption for mixtures of selected water solutions of dye baths and assistants.

Three different concentrations of the mixture have been tested, i.e., 0.1%, 0.5%, 3.0%. See Table 1.

TABLE 1. CONCENTRATION OF POLLUTANTS CONTAINED IN AQUEOUS SOLUTIONS OF DYEING BATHS AND ASSISTANT MIXTURES

Component	Concentration in aqueous solution of dyeing bath mixture, mg/dm^3		
	0.1%	0.5%	3.0%
Dyes			
Aniline red BLN	4.17	20.85	125.1
Lunasol rot 5B	5.00	25.00	150.0
Sulfur brown	3.34	16.70	100.0
Welan brown	6.67	33.35	200.0
Total dyes concentration	19.18	95.90	575.1
Assistants			
Dispersing agent NNO	2.00	10.00	60.0
Elanofor anionic detergent	0.33	1.65	10.0
Lodegal MK - anionic detergent	1.67	8.35	50.0
Rokafenol N8 - nonionic detergent	0.66	3.30	19.8
Siarczanol N2 - sulfate ester detergent	0.08	0.40	2.4
Fixative WOM - cationic detergent	6.67	3.35	200.0
Total assistants concentration	11.41	57.05	342.2
Others			
Acetic acid	10.00	50.0	300.0
Sodium sulfide	8.35	41.75	252.0
Sodium carbonate	8.35	41.75	252.0
Sodium sulfate	8.00	40.00	240.0

TABLE 2. CONCENTRATION OF POLLUTANTS CONTAINED IN AQUEOUS SOLUTIONS OF DYEING BATHS USED IN TREATMENT PROCESS STUDY BY ADSORPTION METHOD

Tested dyeing bath	Concentration of tested dyeing bath %	Components of dyeing bath	Component concentration mg/dm^3
Metallic-complex dyeing bath	10	Dye - Polfalan GL brown	2500
		Acetic acid	3000
		Rokamina S-22	100
		Sulforokanol 0-100	200
		Rokacet	2000
Sulfur dyeing bath	5	Dye - Schwefelneu blau FBL 133	2000
		Calcined soda	3000
		Siarczanol	50
		Mirabilite	10000
Acid-chrome dyeing bath	0.5	Dye - Acid-chrome blue ERN	150
		Acetic acid	100
		Potassium dichromate	50
		Sulforokanol 0-100	150
Direct dyeing bath	5	Dye - Direct brown B	1000
		Calcined soda	25
		Rokafenol N8	50
Reactive dyeing bath	1	Dye - Helaktyn red F_4 BAN	300
		Calcined soda	200
		Mirabilite	600
		Rokafenol N8	20
Basic dyeing bath	5	Dye - Aniline blue RL 50/100	1250
		Acetic acid	1500
		Rokafenol N8	50
Dispersed dyeing bath	5	Dye - Synten blue P-BL	3000
		Sulforokanol 0-100	100

(continued)

Table 2 cont.

Tested dyeing bath	Concentration of tested dyeing bath %	Components of dyeing bath	Component concentration mg/dm^3
Mixture of above mentioned dyeing bath	1	Dyes - Total	328.40
		Polfalan brown GL	35.70
		Schwefelneu blau FBL 133	57.10
		Acid-chrome blue ERN	42.80
		Direct brown B	28.60
		Helaktyn red F_4 BAN	42.80
		Aniline blue RL 50/100	35.70
		Synten blue P-BL	85.70
		Assistants - Total	85.67
		Rokamina S-22	1.43
		Sulforokanol 0-100	48.60
		Rokacet	28.50
		Siarczanol N-2	1.43
		Rokafenol N8	5.71
		Acetic acid	114.27
		Calcined soda	115.00
		Mirabilite	371.42
		Potassium dichromate	14.29

For investigations of wastewater treatment by activated sludge method, municipal wastewaters were used with the addition of selected pollutants typical for dyeing wastewater. In tests on wastewater treatment by activated sludge, municipal wastewaters mechanically untreated were used with addition of one selected substance with the concentration of 300 mg/dm^3. Tested for their influence on activated sludge were lunasol rot 5B, special basic red BLN, sulfur brown, welan brown, dispersing agent NNO, and fixing agent WOM. Laboratory investigations of wastewater treatment by activated sludge method in continuous system were carried out for two different compositions of wastewater:

(1) Municipal wastewater primarily treated (2 hours sedimentation) with the addition of six selected wastewater components at concentration of 50 mg/dm^3 of each. Total concentration of selected components was 300 mg/dm^3. These compounds have previously been treated individually.

(2) Municipal wastewater primarily treated (2 hours sedimentation) with the addition of mixture of the selected solutions of dye baths, and assistants. The investigations were carried out for 0.1 percent solution of selected mixture in municipal wastewater. The mixture was composed of solutions of the following dyes and assistants:

reactive dye	- lunasol Rot 5B
basic dye	- special basic red BLN
welan dye	- welan brown
sulfur dye	- sulfur brown
fixing agent WOM	
dispersing agent NNO	

Total concentration of dyes and assistants reached about 30 mg/dm^3.

For batch tests of wastewater treatment by anaerobic digestion, municipal wastewater untreated mechanically was used with addition of one selected substance with the concentration of 300 mg/dm^3, similar to the tests on wastewater treatment by activated sludge method.

In laboratory investigations on continuous wastewater treatment by the anaerobic digestion method using biological filters, municipal wastewater treated mechanically was used with the addition of reactive dye - lunasol Rot 5B with concentration of 300 mg/dm^3.

In test investigations on the influence of selected pollutants contained in dyeing wastewater on the course of anaerobic digestion process of wastewater sludges, the wastewater sludges from primary sedimentation tanks were used with the addition of one selected component or mixture of dye baths. For each added substance as well as for the mixture, the influence of different concentrations was studied.

The components added in particular tests are listed in Tables 3 and 4.

TABLE 3. CONCENTRATION OF POLLUTANTS - COMPONENTS OF DYEING WASTEWATERS CONTAINED IN SEWAGE SLUDGE USED IN INVESTIGATION ON ANAEROBIC DIGESTION PROCESS

Series number	Component	Concentration of component g/dm^3		
I	Reactive dye - Lunasol	3.0	10.0	25.0
III	rot 5B	0.3	1.0	3.0
I	Dispersed dye - Polanit rot BRL -	3.0	10.0	25.0
III	Synten yellow	0.3	1.0	3.0
I	Basic dye - Aniline red BLN	3.0	10.0	30.0
III		0.3	1.0	3.0
I	Metallic - complex dye	3.0	10.0	30.0
III	- Polfalan green 2 BL	0.3	1.0	3.0
II	Direct dye	0.3	1.0	10.0
III	- Helion yellow BRL	3.0	6.0	
II	Acid dye - Folan red B	0.3	1.0	10.0
III	- Folan red B	3.0	6.0	
II	Acid chrome dye -	0.3	1.0	10.0
III	- acid chrome red B	3.0	6.0	
II	Sulfur dye -	0.3	1.0	10.0
III	- Sulfur brown	3.0	6.0	
II	Special dye for wool	0.3	1.0	10.0
III	dyeing - Lasting red PGL	3.0	6.0	
II	Welan dye - Welan brown	0.3	1.0	10.0
II	Assistant - Dispersor NNO	0.3	1.0	10.0
II	Assistant - Fixative WOM	0.3	1.0	10.0
III		3.0	6.0	
II	Assistant - Elanofor	0.3	1.0	10.0
III	Mixture of dyeing bath	0.3	1.0	5.0

TABLE 4. CONCENTRATIONS OF CONTAMINANTS CONTAINED IN THE AQUATIC SOLUTIONS OF DYEING BATHS MIXTURES

Components of dyeing bath	Concentration of component in aquatic solutions of dyeing bath mixture, mg/dm^3		
	0.3%	1.0%	5.0%
Dyes:			
Aniline red BLN	12.51	41.7	208.5
Lunasol rot 5B	15.00	50.0	250.0
Sulfur brown	10.02	33.4	167.0
Welan brown	20.01	66.7	333.5
Total dye concentration	57.54	191.8	959.0
Assistants:			
Dispersing agent NNO	6.0	20.0	100.0
Elanofol - anionic detergent	0.99	3.3	16.5
Lodegal MK - anionic detergent	5.01	16.7	83.5
Rokafenol N8 - nonionic detergent	1.98	6.6	33.0
Siarczanol N2 - sulfate ester detergent	0.24	0.8	4.0
Fixative WOM - cationic detergent	20.01	66.7	333.5
Total assistants concentration	34.23	114.1	570.5
Others:			
Acetic acid	30.0	100.0	500.0
Sodium sulfide	25.05	83.5	417.5
Sodium carbonate	25.04	83.5	417.5
Sodium sulfate	24.0	80.0	400.0

SECTION 5

PHYSICAL AND CHEMICAL TREATMENT METHODS OF DYEING WASTEWATERS

5.1 COAGULATION

Methodology and Scope of the Investigation

The purpose of the technological investigations was to determine the efficiency of dyeing wastewater treatment using the coagulation method. The investigations were carried out on laboratory scale using aluminium and ferrous sulfates as coagulants with pH adjustment in the range from 8 - 12, with solution of CaO. In addition, coagulation tests were accomplished using $FeCl_3$ at pH of 8.0 and $Al_2(SO_4)_3$ at pH = 6.8. Also tests of coagulation using fly ashes were carried out , and tests on the coagulation using $Al_2(SO_4)_3$ or $FeCl_3$ with assistance of fly ashes. Additionally the influence of pH ranging from 11.96 to 13.00 on coagulation efficiency with the use of CaO was studied.

The investigations were carried out for dyeing wastewater composed of synthetically prepared mixture of various dye baths, according to the recipe applied at textile manufacturing plants.

The criterion of selection of appropriate dye groups, as well as assistants for the dye baths, was the applicability of a given component in technological processes of the textile industry.

Tests were carried out using the equipment in static conditions.

To obtain optimum conditions of the process, the coagulation was accomplished on large laboratory scale using 35 liters of wastewater of 3 percent concentration.

Both in tests and in laboratory investigations, the following duration times for the individual stages of coagulation were used:

rapid mixing	- 3 min
slow mixing	- 20 min
sedimentation	- 120 min

Mechanical mixers were used for rapid and slow mixing in test investigations, while on large laboratory scale examinations, compressed air was applied.

The coagulation process was performed at ambient temperature and in addition for coagulation using CaO also at the temperature of 95 °C.

To establish the efficiency of the coagulation process, the following physical and chemical determinations in wastewater samples were carried out before and after coagulation: pH, temperature, color, turbidity, the volume of precipitated sludge (cm^3/dm^3) after 2 hours sedimentation.

The tests run are presented in Table 5.

Discussion of the Results

Coagulation of dyeing wastewater was carried out mainly in order to remove color and turbidity from these wastewaters. Considering the high variety of the dyes and assistants used, reports were encountered containing extremely different conclusions concerning treatment effects of the coagulation process. Also, the mechanism of color removal was not yet sufficiently explained. Zuckermann and Molof (1) suggested that chemical hydrolysis takes place after the addition of calcium hydroxide and increased pH. Zuckermann and Molof (1) stated that chemical hydrolysis changes high molecular organic molecules (dyes) into low molecular ones.

In the light of Zuckermann's and Molof's statements (1), of special concern in the investigation was the effects of color removal as a result of lime addition to dyeing wastewater solution.

The tested solution of dyeing wastewater was composed of, as it was previously stated, four dyes from each of the groups of reactive, basic, welan and sulfur dyes.

Reactive dyes are characterized by good water solubility and quite easily hydrolyze turning into insoluble form. Hydroxyl ions react in water solution with reactive groups of a dye causing its hydrolysis. The hydrolyzed dye cannot react with fiber and can only settle on its surface.

Basic dyes in the form of base are insoluble in water. They form water soluble salts, e.g., hydrochlorides or acetates in reaction with inorganic or organic acids. In water medium these salts dissociate into dyeing cation and anion of acid radical

$$B - NH_2 \cdot HCl \rightleftarrows (B - HN_3)^+ + Cl^-$$

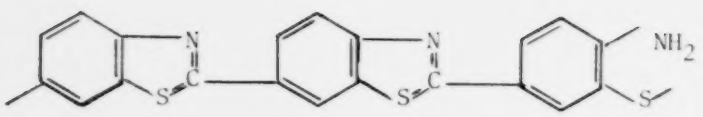
Therefore increasing pH of the solution through lime addition should convert the basic dye into insoluble form and precipitate them from the solution.

Sulfur brown dye used in the investigations is made from the reaction of aromatic amines, and nitrocompounds with sulfur. In its molecule, the thiazole rings are such as:

TABLE 5. LIST OF TESTED CONDITIONS OF COAGULATION

Coagulant	Tested mixture of dyeing wastewater					
	0.1%		0.5%		3%	
	Dose mg/dm^3	pH adjustment	Dose mg/dm^3	pH adjustment	Dose mg/dm^3	pH adjustment
1. CaO	100-10000		100-10000		10-10000	
2. $FeSO_4$	20-1500		30-2000		20-5000	
+CaO	300		300		300	
3. $FeSO_4$	20-1500		30-2000		20-5000	
+CaO	400		400		1000	
4. $FeSO_4$	20-1500		30-2000		20-5000	
+CaO	400		4000		8000	
5. $FeSO_4$	20-1500		30-2000		20-5000	
+CaO	1000		6000		10000	
6. $FeSO_4$	20-1500					
+CaO	4000					
6a. $FeSO_4$			30-2000			
+CaO			6000			
7. CaO			300-1000	11.96-12.80	1000	12.20-12.82
8. $CaO+CO_2^x$			300-6000	6.00		
9. $CaO+CO_2^{xx}$			300-6000	7.48		
10. $CaO+CO_2^{xxx}$			300-6000	7.16		
11. $CaCO_3$			300-4000	n.d.		
12. $Al_2(SO_4)_3$			50-2000			
+CaO			4000			
13. $Al_2(SO_4)_3$			10-250	n.d.		
14. $Al_2(SO_4)_3$			10-250	6.8		
15. Fly ashes			50-500			
$+Al_2(SO_4)_3$			50			

x - CO_2 addition before coagulant addition
xx - CO_2 addition after coagulation
xxx - CO_2 addition after coagulation and decantation
n.d. - not determined



Sulfur dyes are usually insoluble in water. In order to convert them into soluble form, they are usually reduced with Na_2S in alkaline medium, and the sodium salt of sulfur dye is formed.

$$B - S - S - B \xrightarrow[red.]{Na_2S} 2B - SH \xrightarrow{alkali} 2B - SNa$$

The reduced form of the dye is oxidized relatively easily with atmospheric oxygen which converts it into the insoluble form.

$$2B - SNa \xrightarrow[oxid.]{O_2} B - S - S - B$$

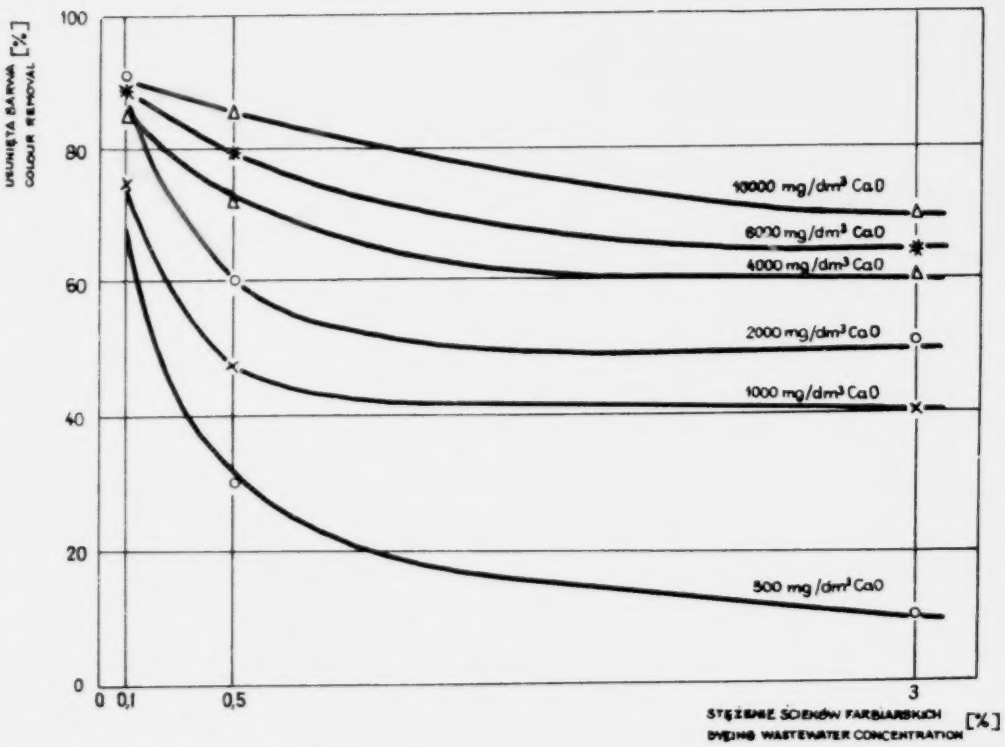
In this investigation it seems that quite a considerable part of the dye was converted into insoluble form during the preparation of all dye bath mixtures. Also, probably part of the sulfur dye oxidizes to insoluble form during subsequent operations of diluting and mixing.

The fourth group of the used dyes, welan dyes, consist of a mixture of dispersed and metallic dyes in the relation 1:2. Molecules of dispersed dyes do not contain sulpho or carboxyl groups. Before use, dyes are converted by dispersing agents into suspension form. Metallic dyes are soluble in water, and this property is due to sulfo group - SO_3H or sulfonamide group - SO_2NH_2. It seems that on account of their structure, welan dyes do not hydrolize, however, they can be removed in coagulation process as a result of adsorption of the dispersed suspended dye and of electrokinetic influence of the coagulant on the anion of metallic dye.

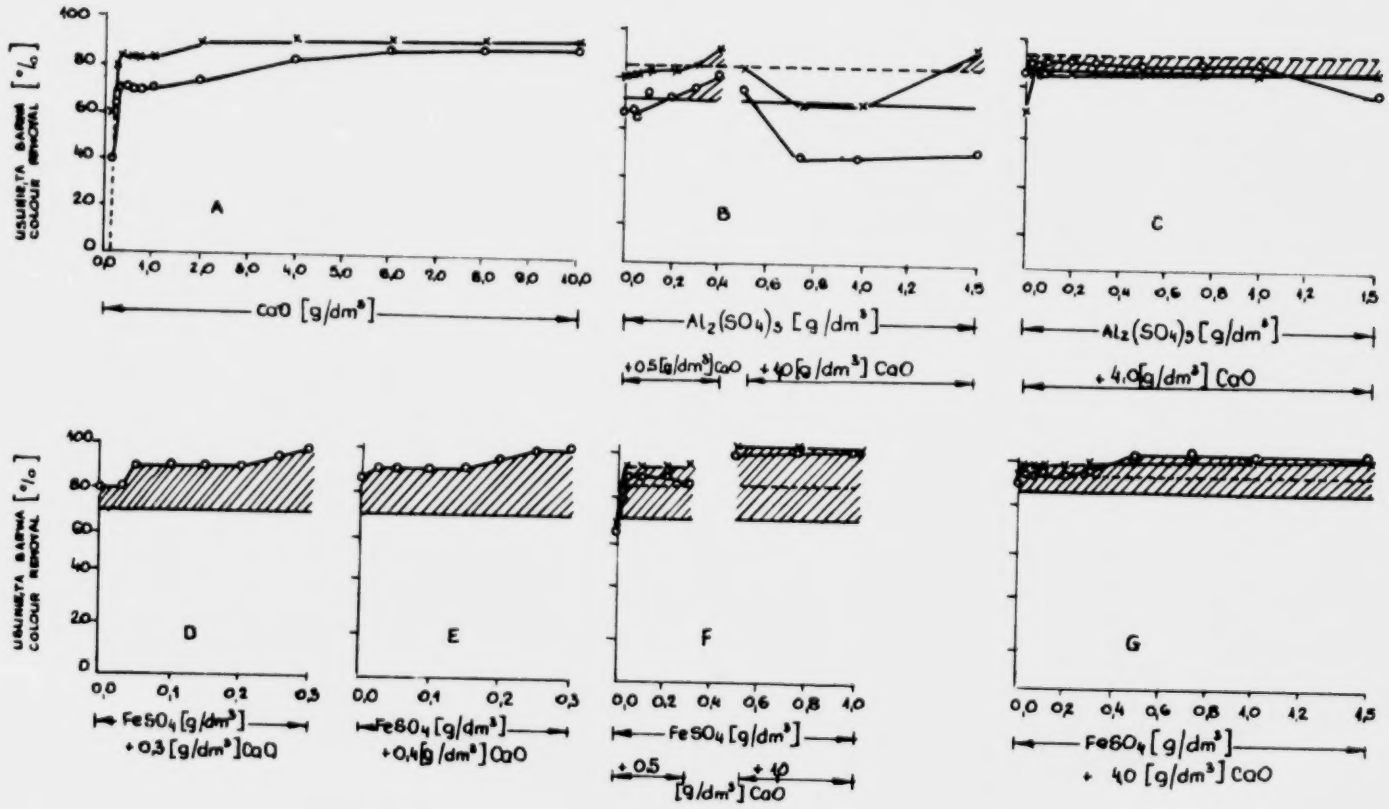
Analysis of dyes composing dye baths were performed after the addition of calcium hydroxide to determine how effectively the color was removed. It was possible to remove a considerable part of color from tested solutions through lime addition. The color removed increases with the increase of lime dose, while it decreases with the increase of dyeing wastewater concentration. This relationship is shown in Fig. 1.

The very distinct decrease of color removal efficiency with the increase of dyeing wastewater concentration prompted deeper analysis of the problem for the individual concentrations.

When presenting the data as it is done in Fig. 2a, the effect of color removal on the dependence of the CaO dose for 0.1 percent solution is clearly seen. There is a very rapid increase of color removal with the increase of coagulant dose. In practice a dose of 0.300 to 0.400 g/dm^3 is quite sufficient for the effective wastewater decolorization.



Rys 1. Efekty koagulacji ścieków farbiarskich różnymi dawkami CaO.
Figure 1. Effect of dyeing wastewaters coagulation with the use of various doses of CaO as the coagulant.



° Barwa (metoda porównań)
Color (comparison method)

x Barwa (metoda rozcieńczeń)
Color (dilution method)

—— Ununięcie barwy (metoda porównań) przy użyciu CaO
Color removal by CaO coagulation (color measured by the comparison method)

---- Usuniecie barwy (metoda rozcieńczeń) przy użyciu CaO
Color removal by CaO coagulation (color measured by dilution method)

Rys 2. Efekt usunięcia barwy w procesie koagulacji 0.1% ścieków farbiarskich.
Figure 2. Color removal by coagulation method 0.1% dyeing wastewaters.

Total color removal by CaO addition was not possible. For a dose of 0.3 to 0.4 g/dm^3 about 83 percent color removal was obtained as determined with the dilution method (Fig. 2a) and for doses from 4.0 to 10.0 g/dm^3 of CaO a constant color removal of 92 percent was obtained.

The addition of aluminum sulfate and ferrous sulfate, coagulants, were studied.

When analyzing Fig. 2b, where the investigations results are presented with CaO addition in a dose of 0.5 and 1.0 g/dm^3, and $Al_2(SO_4)_3$ addition in the range from 0.02 to 1.5 g/dm^3, practically no effects of color removal increase were noted. In fact, extremely strange dyes behaviour was noticed.

While CaO addition in the amount of 4.0 g/dm^3 as it was previously mentioned, 92 percent of color removal was obtained, the additional dose of 0.02 to 1.5 g/dm^3 of $Al_2(SO_4)_3$ did not have any additional influence on the color removal.

The effects of ferrous sulfate addition on the degree of color removal looked somewhat different and the results are shown in Fig. 2d, e, f, and g. The satisfactory color removal was reached with addition of $FeSO_4$ in dose of 0.03 to 0.05 g/dm^3 and with simultaneous addition of CaO in dose of 0.3 to 0.4 g/dm^3. Therefore with a total dose of 0.33 to 0.45 g/dm^3 of coagulant it is possible to remove 90 percent of the color.

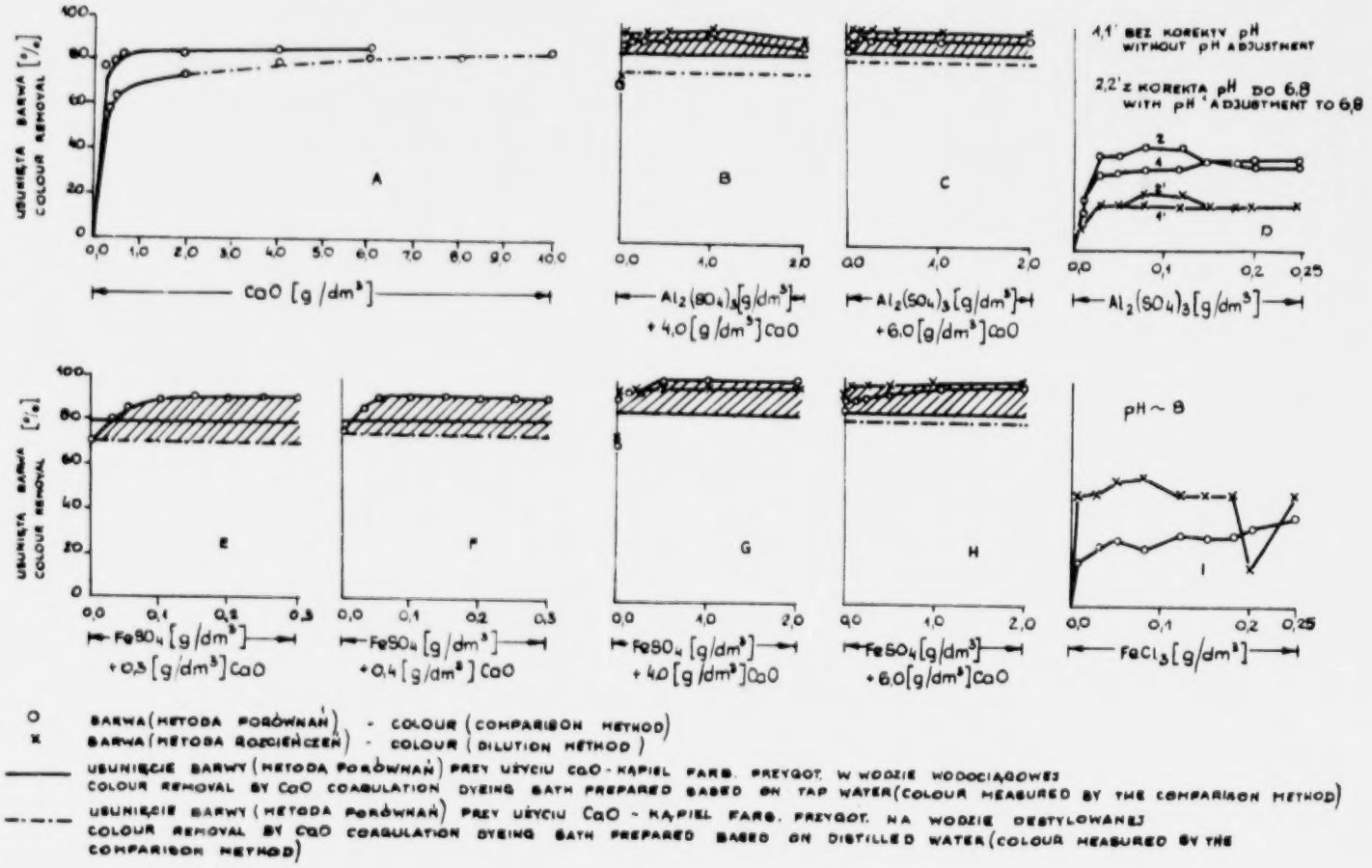
Practically total color removal from 0.1 percent solution of dyeing wastewater was obtained with the addition of 1.0 g/dm^3 of CaO, and $FeSO_4$ addition in a dose of 0.5 g/dm^3 and above. See Fig. 2f and 2g.

When testing the solution of dyeing wastewater of 0.5 percent concentration, the characteristic fact is that with addition of CaO, a similar form of color removal effects was noted (Fig. 3a) as with dyeing wastewater of 0.1 percent concentration.

In contradiction to the effects obtained for a 0.1 percent solution, in case of 0.5 percent solution of dyeing wastewater the addition of aluminum sulfate by coagulation with the dose of 4.0 to 6.0 g/dm^3 of CaO caused quite distinct increase of color removal effect (Fig. 3b and 3c). Maximum effects of color removal with the addition of aluminum sulfate and calcium hydroxide equalled about 96 percent; therefore, total color removal was not obtained.

Besides CaO, when dosing $FeSO_4$, the addition of 0.3 or 0.4 g/dm^3 of CaO and 0.07 to 0.1 g/dm^3 of $FeSO_4$ is considered as the smallest dose leading towards obtaining satisfactory effects. This sums up to be a total addition of coagulants in the range between 0.4 and 0.47 g/dm^3.

Comparing this dose with the one obtained for solution of 0.1 percent of dyeing wastewater, more general conclusions can be drawn that for relatively diluted dye solution, CaO dose of 0.1 g/dm^3 and $FeSO_4$ dose of 0.07 g/dm^3 give effective hydrolysis and coagulation.


USUNIĘTA BARWA [%]
COLOUR REMOVAL
A
CaO [g/dm³]
B
Al₂(SO₄)₃ [g/dm³]
+4,0 [g/dm³] CaO
C
Al₂(SO₄)₃ [g/dm³]
+6,0 [g/dm³] CaO
1,1' BEZ KOREKTY pH
WITHOUT pH ADJUSTMENT
2,2' Z KOREKTA pH DO 6,8
WITH pH ADJUSTMENT TO 6,8
D
Al₂(SO₄)₃ [g/dm³]
E
FeSO₄ [g/dm³]
+0,3 [g/dm³] CaO
F
FeSO₄ [g/dm³]
+0,4 [g/dm³] CaO
G
FeSO₄ [g/dm³]
+4,0 [g/dm³] CaO
H
FeSO₄ [g/dm³]
+6,0 [g/dm³] CaO
pH ~ 8
I
FeCl₃ [g/dm³]
O BARWA (METODA PORÓWNAŃ) - COLOUR (COMPARISON METHOD)
× BARWA (METODA ROZCIEŃCZEŃ) - COLOUR (DILUTION METHOD)
USUNIĘCIE BARWY (METODĄ PORÓWNAŃ) PRZY UŻYCIU CaO - KĄPIEL FARB. PRZYGOT. W WODZIE WODOCIĄGOWEJ
COLOUR REMOVAL BY CaO COAGULATION DYEING BATH PREPARED BASED ON TAP WATER (COLOUR MEASURED BY THE COMPARISON METHOD)
USUNIĘCIE BARWY (METODĄ PORÓWNAŃ) PRZY UŻYCIU CaO - KĄPIEL FARB. PRZYGOT. NA WODZIE DESTYLOWANEJ
COLOUR REMOVAL BY CaO COAGULATION DYEING BATH PREPARED BASED ON DISTILLED WATER (COLOUR MEASURED BY THE COMPARISON METHOD)

Rys 3. Efekt usunięcia barwy w procesie koagulacji 0.5% ścieków farbiarskich.
Figure 3. Color removal by coagulation method 0.5% dyeing wastewaters.

A doubt that the hydrolysis process really takes place was dispelled to a certain degree by examinations of color removal with only the addition of aluminum sulfate to dyeing wastewater solution (Fig. 3d). Investigations with and without pH adjustment to 6.8 showed that above the dose of 0.02 g/dm^3 $Al_2(SO_4)_3$, the color removal was not increased but equal to 40 percent by the comparison method and 20 percent by the dilution method.

Therefore, it can be supposed that a minute part of the dyes is subject to electrokinetic forces during the coagulation process. Also, a hypothesis can be made that there is a lack of sufficient number of colloidal molecules, which during the aggregation process caused simultaneous removal of a part of the dyes in the adsorption process. Such hypothesis results also to some extent from the comparison of literature data with our own investigations (not included in the program of presently reported works) concerning actual existing wastewater. Because for such a type of wastewater, effective coagulation and color removal just by the addition of only aluminum sulfate in relatively low doses to about 0.2 g/dm^3 is very often noted.

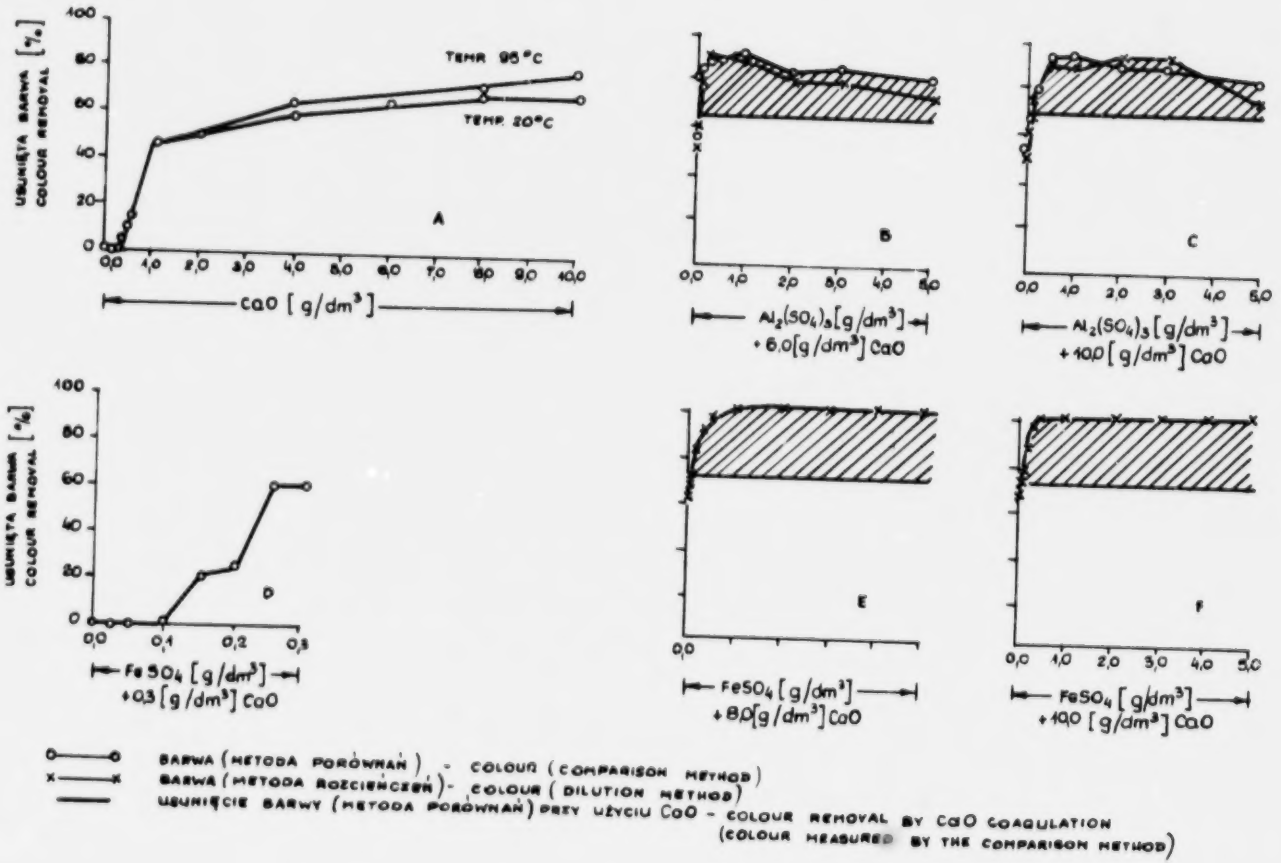
Also, it should be remembered that in actual existing wastewater, a hydrolysis process could take place during mixing various types of wastewater, including those with increased pH.

The importance of chemical processes resulting from alkalizing environment appears to be very important in the case of CaO addition into 3 percent dyeing wastewater solution. When analyzing Fig. 4a, the complete lack of color removal with low doses of CaO can be seen. Only the CaO dose of 1.0 g/dm^3 causes considerable color removal of 45 percent. The color removal increases to the value of 70 percent together with the increase of CaO dose to 10.0 g/dm^3. Considering the large dose, the color removal effect is little. Trials have been undertaken of increasing color removal by raising temperature up to 95 °C in the coagulation process (hydrolysis) by means of CaO. However, no positive effects were obtained, because the increase of color removal was only 10 percent.

On the other hand, a positive effect of the addition of aluminum sulfate was obtained. With a dose of 6.0 and 10.0 g/dm^3 of CaO (Fig. 4b and 4c) for relatively low doses of $Al_2(SO_4)_3$, a very good decolorization was reached with 96 percent of color removal.

Similarly, perfect effects of color removal were obtained through joint action of calcium hydroxide and $FeSO_4$ (Fig. 4e and 4f). However, this effect was possible with only very large doses of CaO above 6.0 g/dm^3. Fig. 4e and 4f show that color removal of 99 percent is possible either with the dose of 8.0 g/dm^3 of CaO and 1.0 g/dm^3 of $FeSO_4$ or with the dose of 10.0 g/dm^3 of CaO and 0.5 g/dm^3 of $FeSO_4$.

In compliance with suppositions arising from the analysis of properties of tested dyes, as a result of hydrolysis connected with CaO addition to dyeing wastewater solutions, the individual dyes removal takes place in various degrees. This fact is stated on the basis of observations of color



Rys 4. Efekt usunięcia barwy w procesie koagulacji 3% ścieków farbiarskich.
Figure 4. Color removal by coagulation method 3% dyeing wastewaters.

tint changes of coagulated sample, in comparison with standards prepared by dilution.

It can be considered that additional proof for hydrolysis process resulting from CaO addition to wastewater is a complete lack of color removal in case of the addition of calcium carbonate to dyeing wastewater solution.

Joint action of calcium hydroxide and ferrous sulfate, ferrous chloride, or aluminium sulfate was found to be indispensable for turbidity removal from wastewater. See Fig. 5, 6, and 7.

However, some exceptional cases were recorded. For a dose of 4.0 g/dm^3 of CaO together with increasing amounts of aluminum sulfate, a decrease of turbidity removal was obtained both for 0.1 and 0.5 percent of dyeing wastewater solution. See Fig. 5c and 6a. Also for the same dose of CaO 4.0 g/dm^3, addition of $FeSO_4$ gave a high efficiency of coagulation, while for other doses of CaO, only a very small positive effect on turbidity removal was noted. See Fig. 5g.

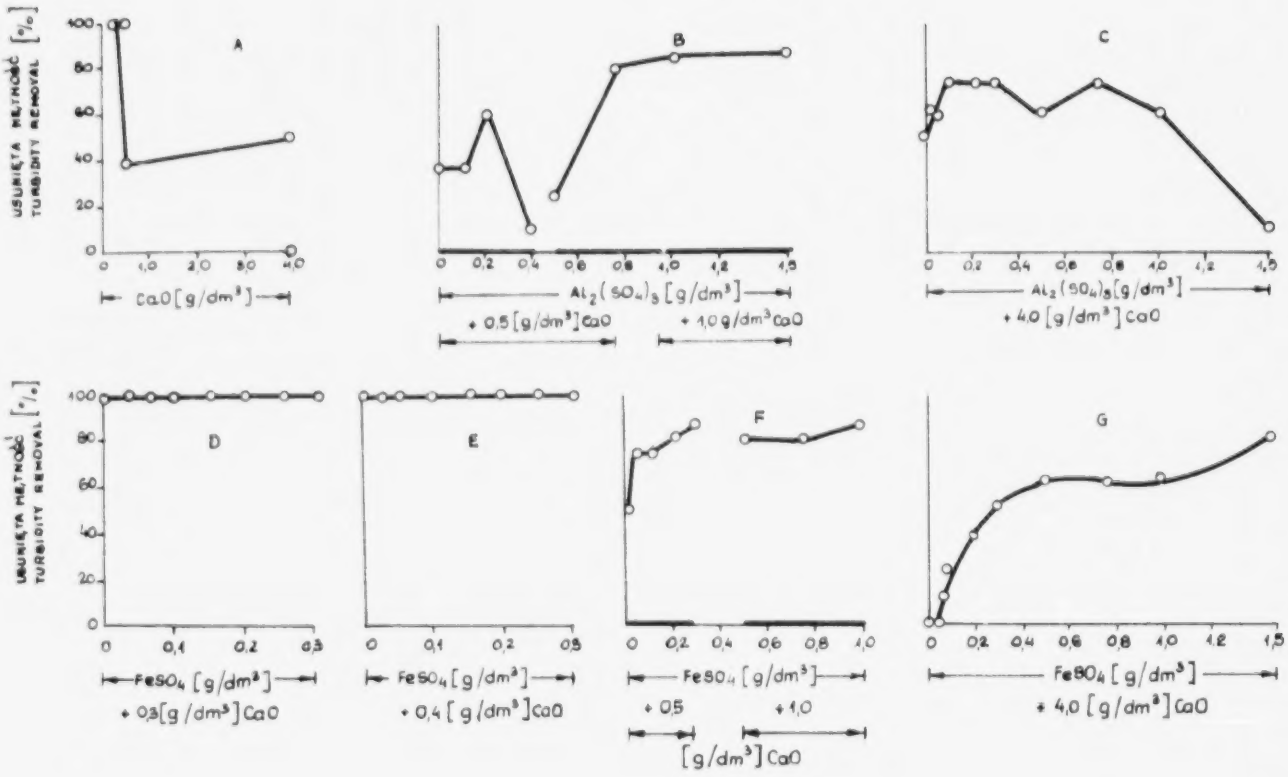
Increasing pH from 11.96 to 13.00 for solutions of 0.1, 0.5 and 3.0 percent concentrations, into which 0.3 or 1.0 g/dm^3 of CaO had been introduced before, very small changes of color removal were obtained. Changes of color removal determined by the comparison method for 0.1 percent solution amounted to $\pm$ 2 percent. For 0.5 percent the differences in color removal were a maximum of 8 percent. The obtained effect of pH increase in coagulated wastewater with CaO addition is presented in Fig. 8.

Changing pH of dyes solution before their coagulation by means of carbon dioxide saturation of the wastewater does not change the treatment efficiency in comparison with samples not undergoing CO_2 saturation. The comparison of the obtained results are presented in Fig. 9 and 3a.

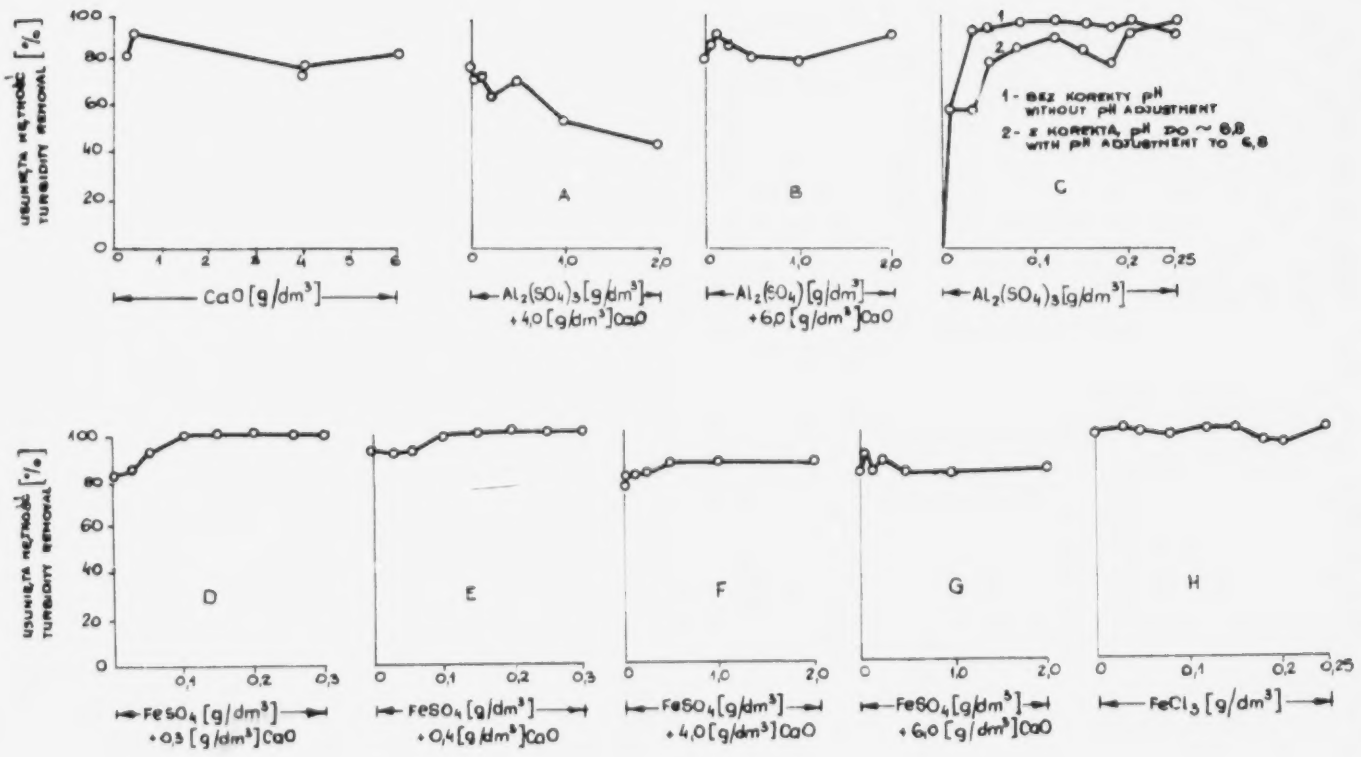
On the other hand, neutralization to pH = 7.6 after separation of the precipitate resulting from the coagulation of the wastewater, certain increase of color removal was noticed. Therefore, it can be stated with a full certainty, that CaO addition and pH increase resulting from it causes permanent changes in dyes structure and properties. Calcium carbonate precipitating during wastewater neutralization process contributes additionally to wastewater clarification. This effect amounts to turbidity removal equaling at least to 90 percent. See Fig. 10. Probably part of the dyes are being absorbed on $CaCO_3$ suspension.

Toward further explanation of the phenomenon taking place in the coagulation process by means of CaO, a stage of free mixing with CO_2 gas until pH reached neutral was carried out. The results presented in Fig. 11 show explicitly a distinct setback of the dyes removal process. Calcium carbonate generated in the CO_2 saturation process eliminated free hydroxide ions from the solution.

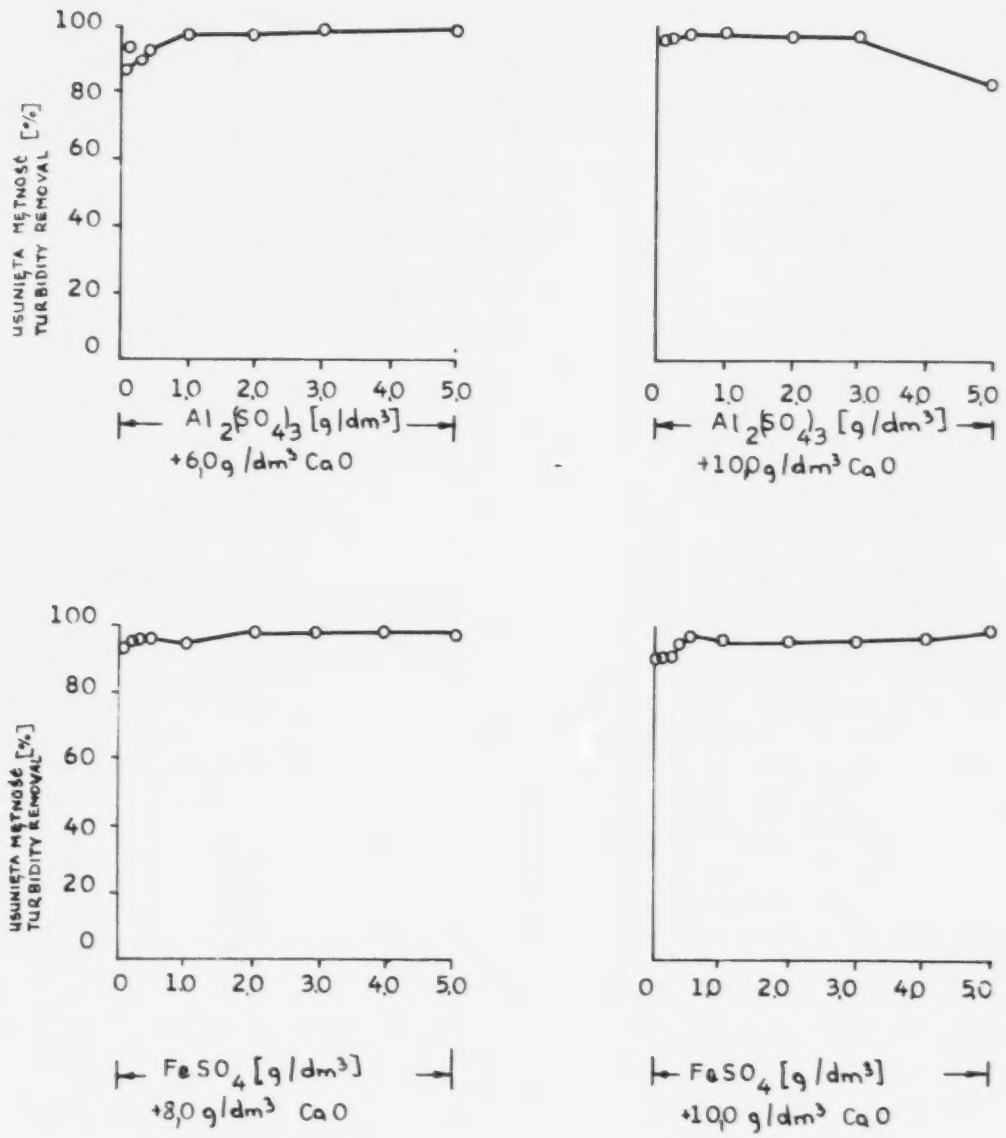
The addition of fly ashes in the range of 0.05-0.5 g/dm^3 into wastewater coagulated with $FeCl_3$ or $Al_2(SO_4)_3$ was studied. For tested doses no substantial color removal was noted, as shown in Fig. 12.



Rys 5. Efekt usuniecia metnosci w procesie koagulacji 0.1% sciekow farbiarskich.
Figure 5. Turbidity removal by coagulation method 0.1% dyeing wastewaters.

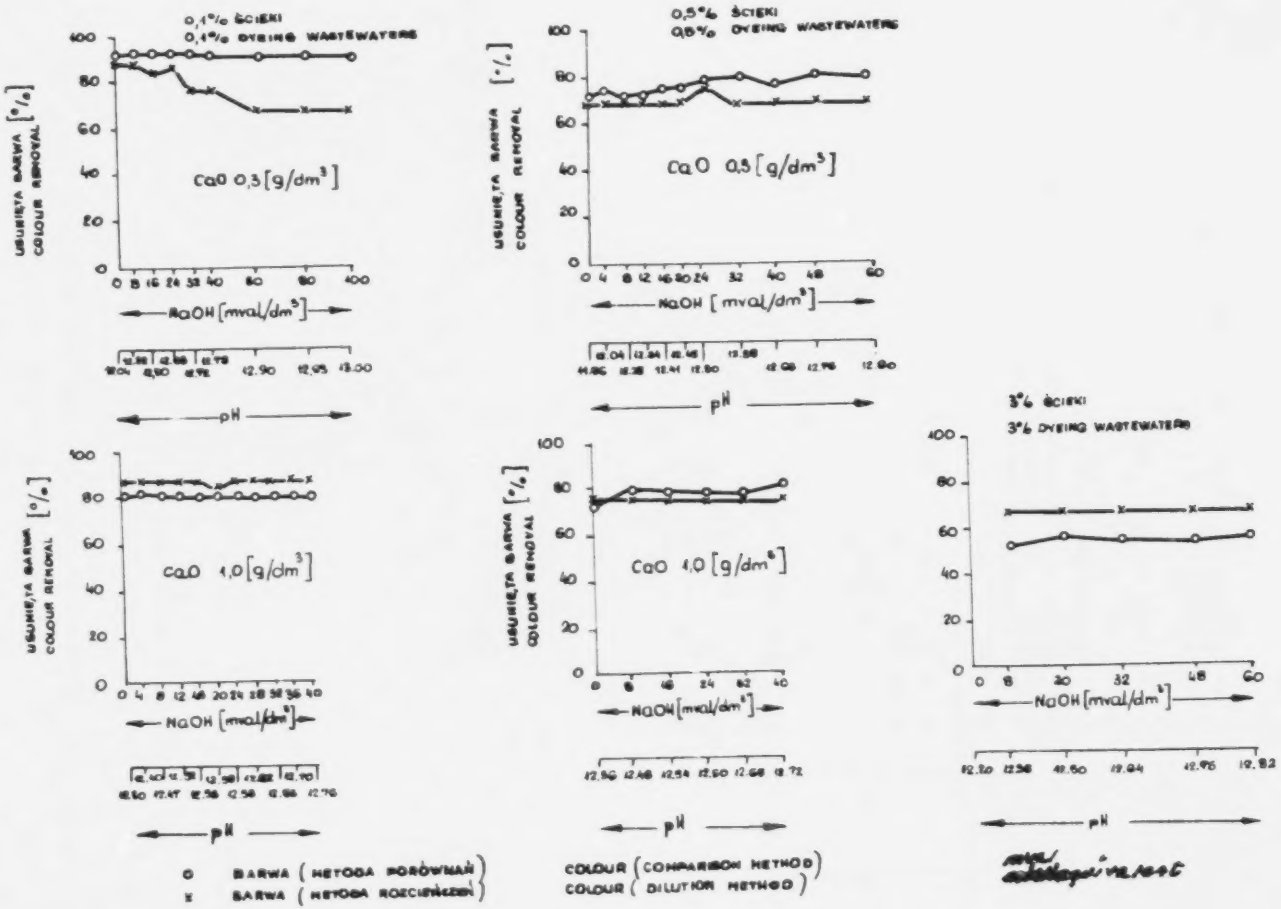


Rys 6. Efekt usunięcia mętności w procesie koagulacji 0.5% ścieków farbiarskich.
Figure 6. Turbidity removal by coagulation method 0.5% dyeing wastewaters.

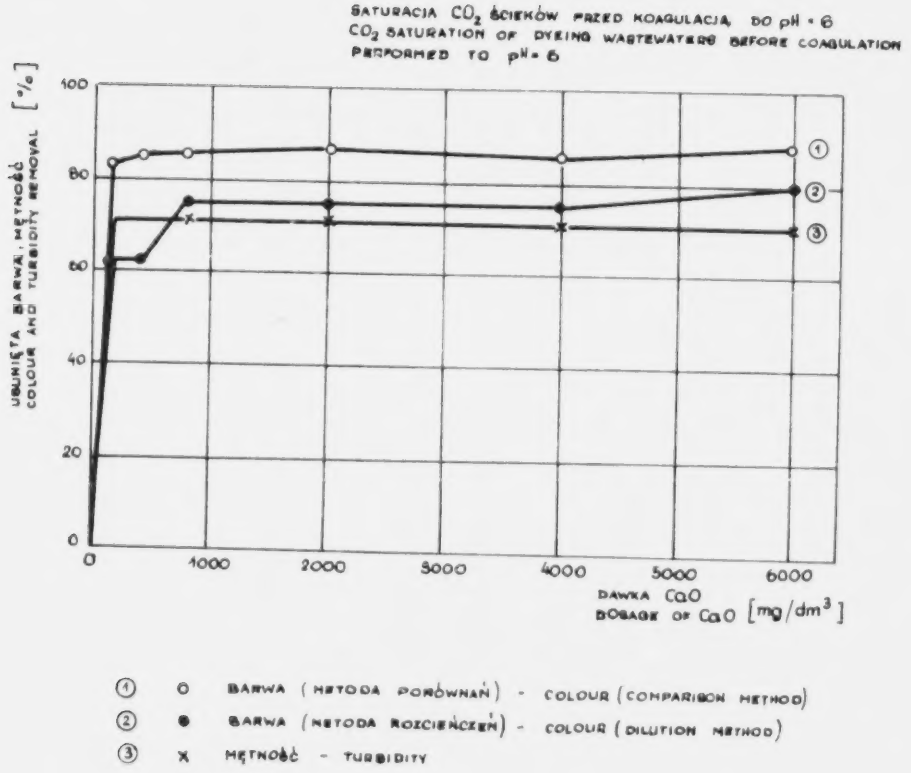


Rys 7. Efekt usunięcia mętności w procesie koagulacji 3% ścieków farbiarskich.

Figure 7. Turbidity removal by coagulation method 3% dyeing wastewaters,

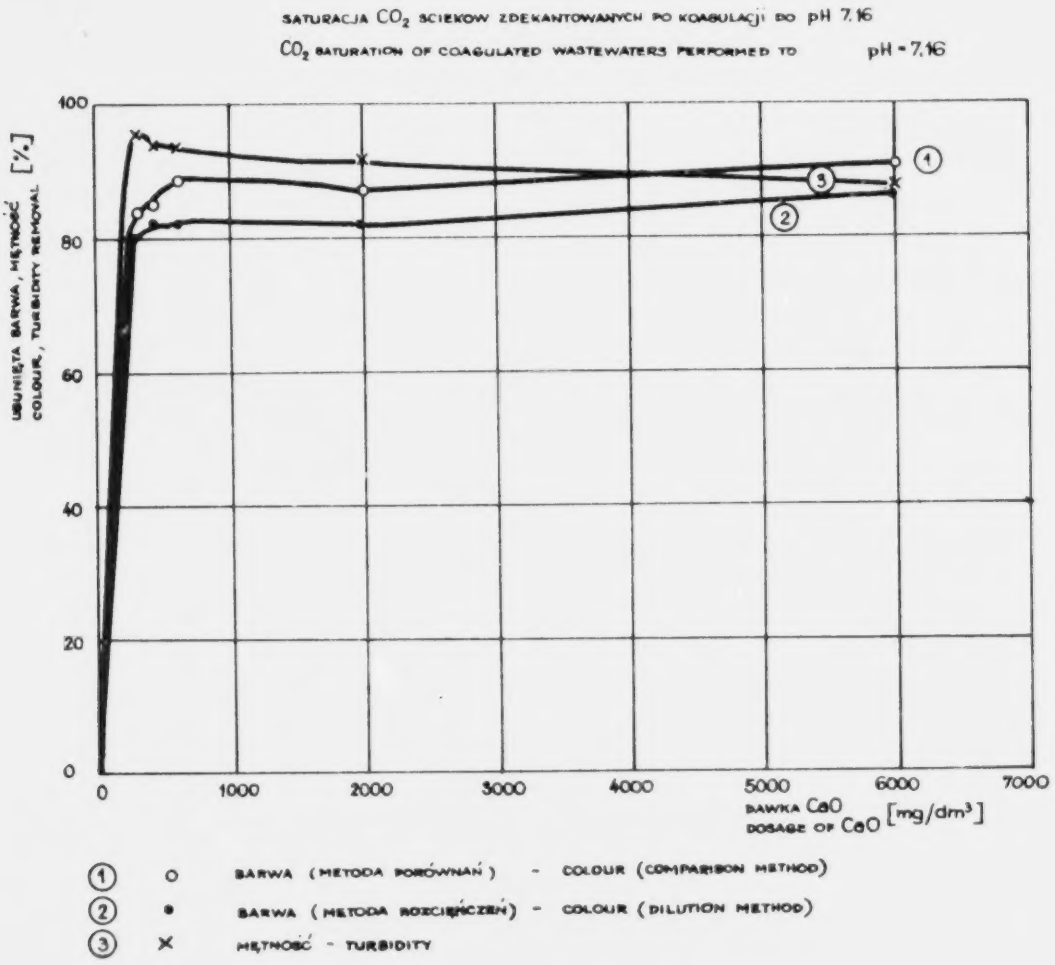


Rys 8. Wpływ podwyższania wartosci pH na uzyskane efekty usunięcia barwy.
Figure 8. Color removal by coagulation method effect of pH adjustment.



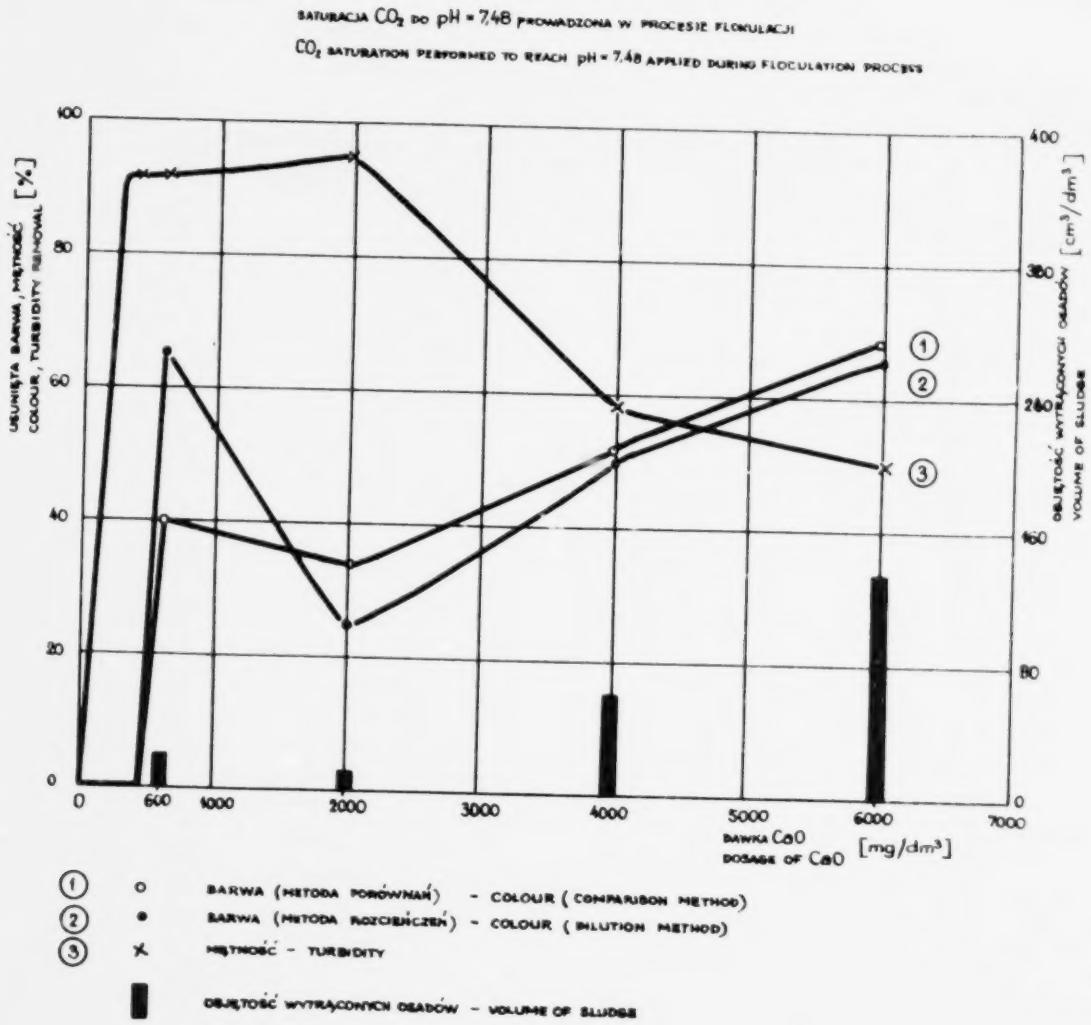
Rys 9. Efekt oczyszczania 0.5% ścieków farbiarskich w procesach saturacji CO_2 i koagulacji różnymi dawkami CaO.

Figure 9. Effects of 0.5% dyeing wastewaters treatment process by CO_2 saturation and coagulation using various CaO doses.



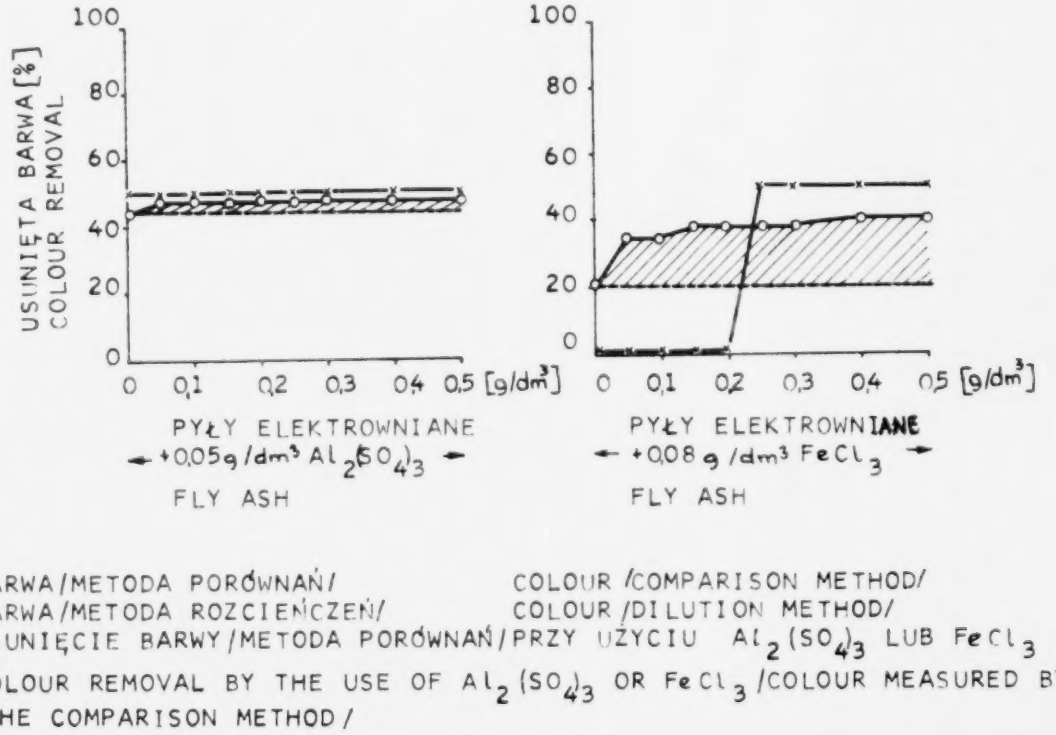
Rys 10. Efekt oczyszczania 0.5% ścieków farbiarskich w procesach koagulacju różnymi dawkami CaO i saturacji CO_2.

Figure 10. Effects of 0.5% dyeing wastewaters treatment process by coagulation using various CaO doses and by CO_2 saturation.


SATURACJA CO_2 DO pH = 7,48 PROWADZONA W PROCESIE FLOKULACJI
CO_2 SATURATION PERFORMED TO REACH pH = 7,48 APPLIED DURING FLOCULATION PROCESS
USUNIĘTA BARWA, MĘTNOŚĆ [%]
COLOUR, TURBIDITY REMOVAL
OBJĘTOŚĆ WYTRĄCONYCH OSADÓW [cm³/dm³]
VOLUME OF SLUDGE
DAWKA CaO [mg/dm³]
DOSAGE OF CaO
BARWA (METODA PORÓWNAŃ) - COLOUR (COMPARISON METHOD)
BARWA (METODA ROZCIEŃCZEŃ) - COLOUR (DILUTION METHOD)
MĘTNOŚĆ - TURBIDITY
OBJĘTOŚĆ WYTRĄCONYCH OSADÓW - VOLUME OF SLUDGE

Rys 11. Efekt oczyszczania 0.5% ścieków farbiarskich w procesie koagulacji różnymi dawkama CaO wspomaganej saturacja CO_2.

Figure 11. Effects of 0.5% dyeing wastewaters treatment process by CaO coagulation and CO_2 saturation simultaneously used.



Rys 12. Efekt usunięcia barwy w procesie koagulacji 0.5% ścieków farbiarskich
Figure 12. Color removal by coagulation method 0.5% dyeing wastewaters

In order to determine the efficiency of detergent and assistants removal by coagulation using 6.0 g/dm^3 of lime milk, the tests were accomplished for 0.5 percent water solutions of the individual substances. The results of the tests evaluated on the basis of COD showed 2.5-5 percent removal of: Lodegal MK, dispersing agent NNO, Rokamin S22, and 12.3 percent for Sulfanol N2 and 22.4 percent for Elanofor.

When repeating selected cases of test investigations in larger scale equipment of the volume of 35 dm^3, similar effects of treatment were recorded with both higher and lower effects. Control tests on large laboratory scale were accomplished for 3 percent solutions of dyeing wastewater.

Treatment effects were examined for three cases:

1. CaO - 6.0 g/dm^3
2. CaO - 8.0 g/dm^3
   + $FeSO_4$ 0.5 g/dm^3
3. CaO - 6.0 g/dm^3
   + $Al_2(SO_4)_3$ 0.25 g/dm^3

The effects of color and turbidity removal obtained during wastewater coagulation using lime milk in a dose of 6.0 g/dm^3 accomplished on laboratory scale were a little higher and equaled to: 80 percent of color and 99.6 percent of turbidity removal. The achieved increase of treatment can be explained most probably by a better mixing of wastewater by means of compressed air.

The effects of coagulation using $FeSO_4$ and CaO defined by color reduction were slightly lower by 9 percent from these obtained in the tests and reached 90 percent of color removal. The efficiency of turbidity removal was high and reached practically 100 percent.

The efficiency of wastewater coagulation with $Al_2(SO_4)_3$ as a coagulant and CaO defined by color reduction increased by 5 percent from the tests results and reached 95 percent.

The sludges produced due to wastewater coagulation by using the three following coagulants were studied:

1.5% of volume - CaO as coagulant

9.0% of volume - using $FeSO_4$ + CaO as coagulant

4.0% of volume - using $Al_2(SO_4)_3$ + CaO as coagulant.

Sludges generated in coagulation were characterized by a low resistance coefficient to filtration. Dewatering feasibility of these sludges was described in Table 6.

TABLE 6. CHARACTERISTICS OF SLUDGE RESULTING FROM COAGULATION PROCESS OF 3% DYEING WASTEWATERS WITH CHOSEN DOSES OF COAGULANTS

Determination	Unit	Coagulant dosage, mg/dm^3		
		CaO 6000	$FeSO_4$ 500	$Al_2(SO_4)_3$ 250
			CaO 8000	CaO 6000
Volume of sludge				
2 h	cm^3/dm^3	15.2	90.9	39.4
6 h	cm^3/dm^3	15.2	63.6	33.3
Total solids	g/dm^3	102.08	52.56	99.17
Volatile total solids	g/dm^3	10.07	17.92	13.17
Volatile total solids	%	9.88	15.1	13.3
Sludge volume index	cm^3/g	9.6	17.9	9.5
Coefficient of specific resistance to filtration	m/kg	$4x10^{11}$	$2.7x10^{11}$	$4.3x10^{11}$
Time of capillary filtration C·S·T	s	96.9	52.1	74.1
Sludge thickening				
0.5 h	cm^3/dm^3	984	-	-
1.0 h	"	960	910	952
2.0 h	"	928	820	892
3.0 h	"	896	710	856
4.0 h	"	872	600	808
5.0 h	"	840	-	768
6.0 h	"	800	530	720
24 h	"	528	390	472
Sludge hydration estimated after 6 h sedimentation	%	88.5	90.7	91.0
Sludge hydration estimated after specific resistance to filtration measurement	%	58.3	63.2	60.9

Considering very high optimum doses of CaO necessary for achieving adequate efficiency of coagulation, the investigations were undertaken concerning possibilities of multiple reuse of lime (2).

- Sludges precipitated after coagulation were dewatered and roasted at a temperature of 550 °C and then reused again for coagulation. This process was repeated twice. The efficiency of pollution removal for primary and secondary treated sludges was similar.

- Sludges precipitated after coagulation were separated from treated wastewater through water decanting and reused as a coagulant for raw wastewater sample. The process was repeated twice, and then sludges were roasted at a temperature of 550 °C.

The roasted sludges were reused for wastewater coagulation, and after four time recycling of hydrated sludge it was roasted again. The roasted sludges were used again for coagulation. The effects of coagulation presented in Fig. 13 proved the feasibility of 7 times recycling of lime with similar efficiency of color removal. The 8th recycling process resulted in 3 times lower efficiency of color removal.

The coagulation process causes COD removal in the range between 10 and 50 percent.

Large amounts of sludges generated in the coagulation process reaching 4 kg/m^3 have an average 90 percent of hydration.

5.2 OZONIZATION

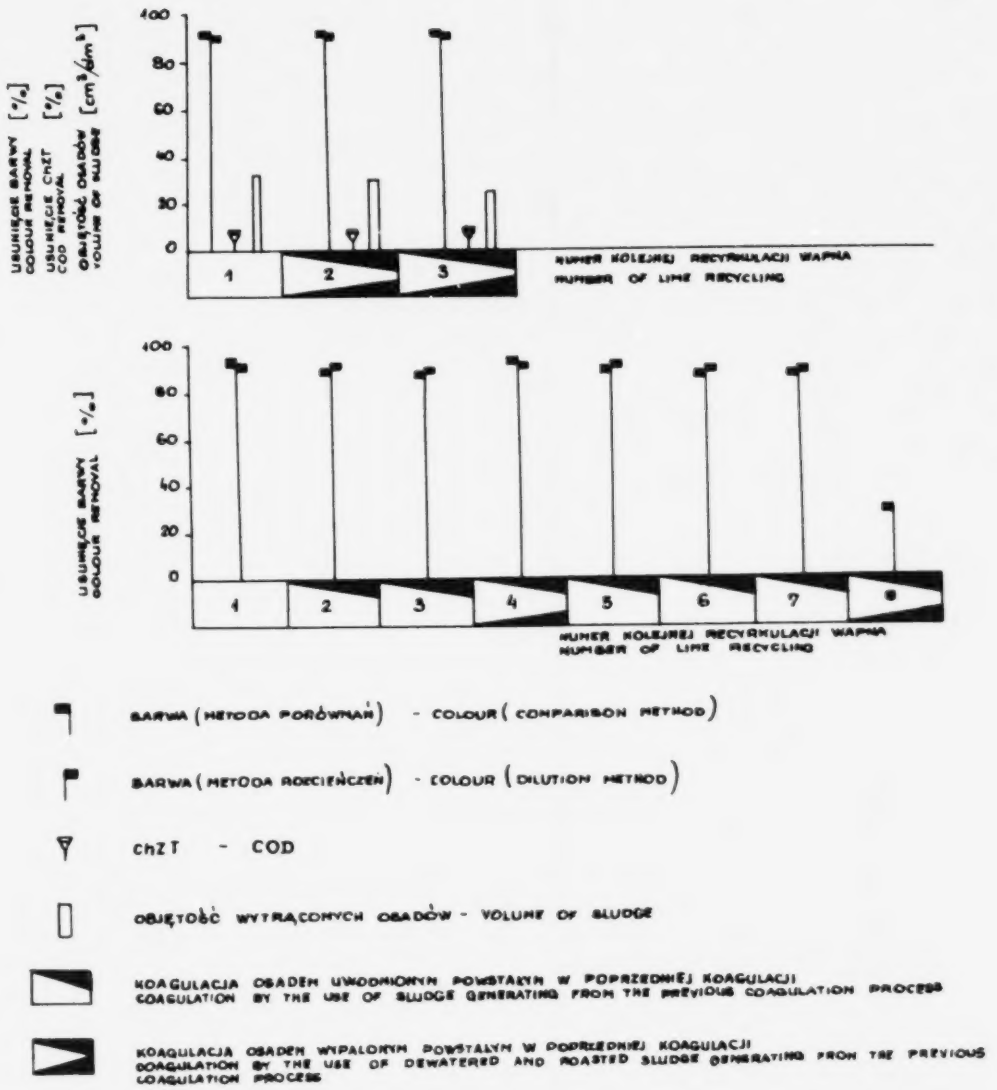
Methods and Range of Investigations

The investigations were directed towards determination of ozonization usability for dyeing wastewater treatment.

Tests were carried out for dyeing wastewater of 0.1 percent and 0.5 percent. In addition, the effects of ozonization were defined for 0.005 percent solutions of individual dyes composing dyeing wastewater. The pH influence was also tested in the range from 3.5 to 12 on ozonization effects for 0.1 percent dyeing wastewater. Tests were carried out in laboratory installations in static conditions. See Fig. 14. Ozone was produced in an ozone generator using air as the oxygen source. Tests were accomplished at ozone generation flow of 2.2 and 9.2 mg/min using ozonization time from 5 to 60 minutes. Ozone was determined quantitatively by the iodometric method. The ozonization effects evaluated were changes in color, COD, and pH.

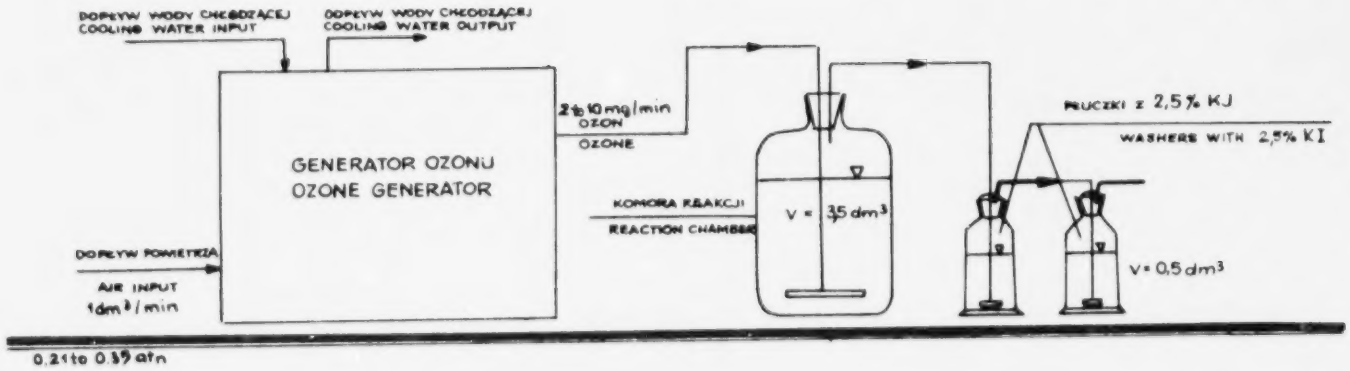
Discussion of Investigations Results

The test investigations showed that color removal is proportional to ozonization time (Fig. 15) and ozone dose (Fig. 16). After 30-minutes contact and at the ozonization flow of 2.2 mg/min, the removed color ranged from 20 percent to 86 percent depending on substrate undergoing tests (Fig. 17). Ozone introduction at a flow of about 9.0 mg/min improved considerably these

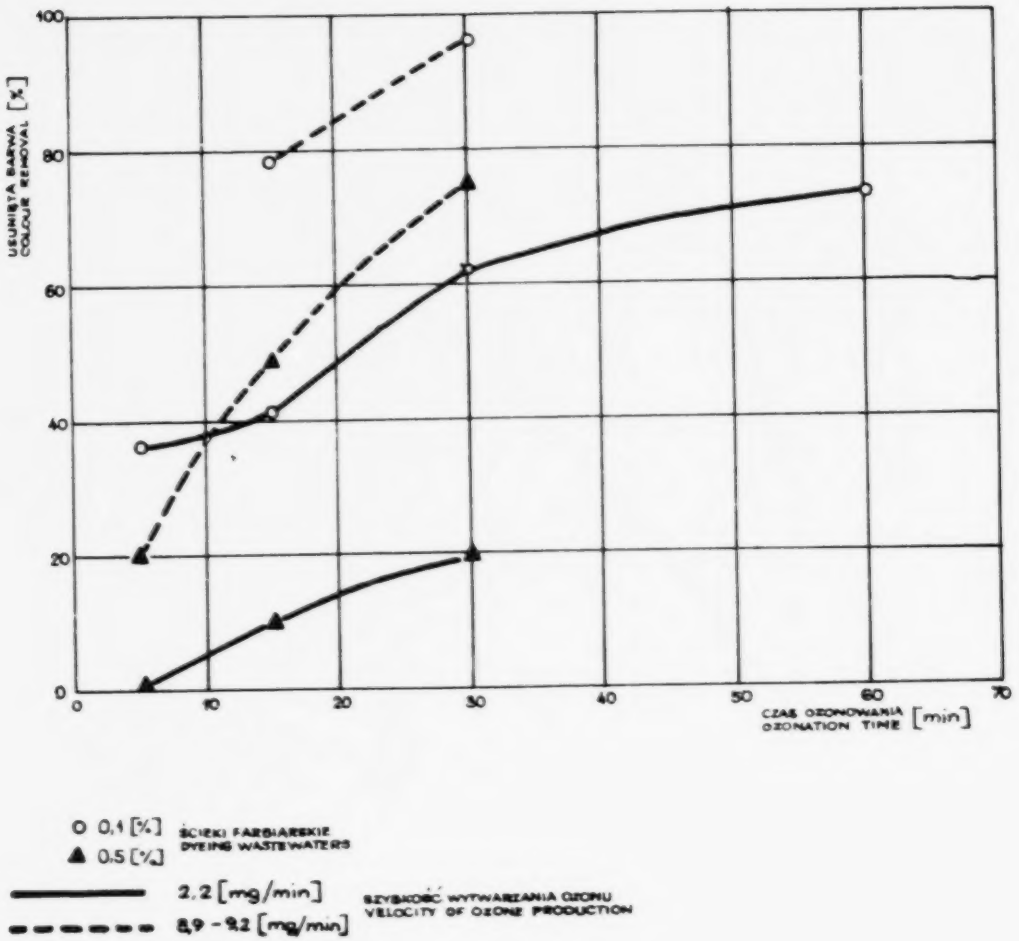

USUNIĘCIE BARWY [%]
COLOUR REMOVAL
USUNIĘCIE ChZT [%]
COD REMOVAL
OBJĘTOŚĆ OSADÓW [cm³/dm³]
VOLUME OF SLUDGE
NUMER KOLEJNEJ RECYRKULACJI WAPNA
NUMBER OF LIME RECYCLING
BARWA (METODA PORÓWNAŃ) - COLOUR (COMPARISON METHOD)
BARWA (METODA ROZCIEŃCZEŃ) - COLOUR (DILUTION METHOD)
ChZT - COD
OBJĘTOŚĆ WYTRĄCONYCH OSADÓW - VOLUME OF SLUDGE
KOAGULACJA OSADEM UWODNIONYM POWSTAŁYM W POPRZEDNIEJ KOAGULACJI
COAGULATION BY THE USE OF SLUDGE GENERATING FROM THE PREVIOUS COAGULATION PROCESS
KOAGULACJA OSADEM WYPALONYM POWSTAŁYM W POPRZEDNIEJ KOAGULACJI
COAGULATION BY THE USE OF DEWATERED AND ROASTED SLUDGE GENERATING FROM THE PREVIOUS COAGULATION PROCESS

Rys 13. Efekty koagulacji 0.1% ścieków farbiarskich przy użyciu CaO świeżego i regenerowanego. Dawka CaO - 6.0 g/dm^3.

Figure 13. Efficiency of the coagulation process performed by the multiple reuse of lime. Dose of CaO to 6.0 g/dm^3 0.1% dyeing wastewaters.

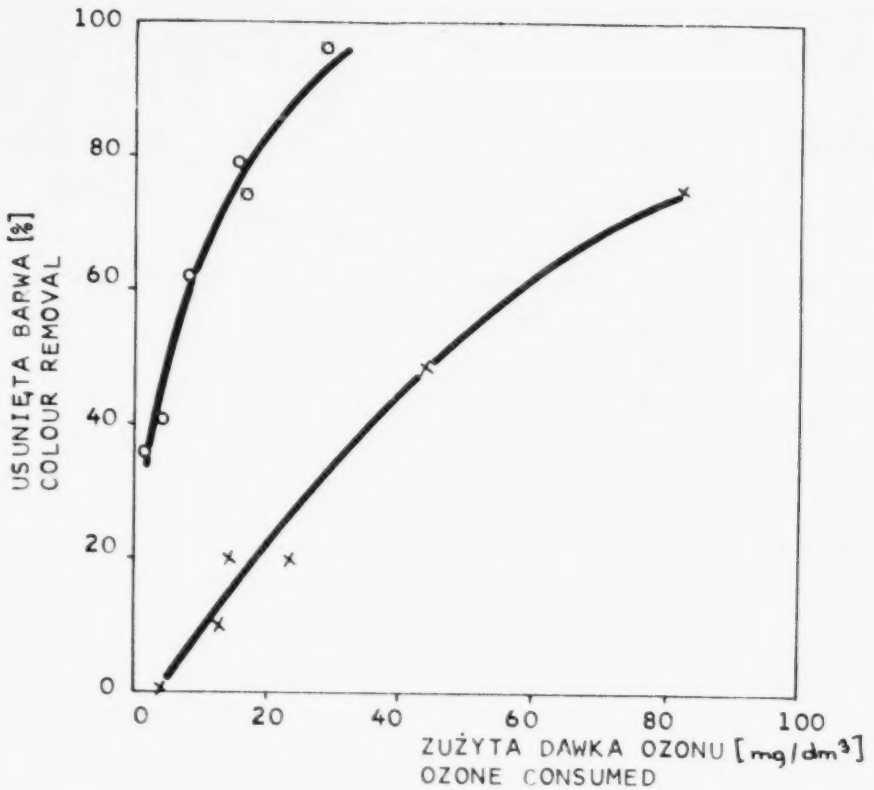


Rys 14. Zestaw aparatury stosowanej do ozonowania ścieków.
Figure 14. Testing equipment for ozonation wastewaters process.



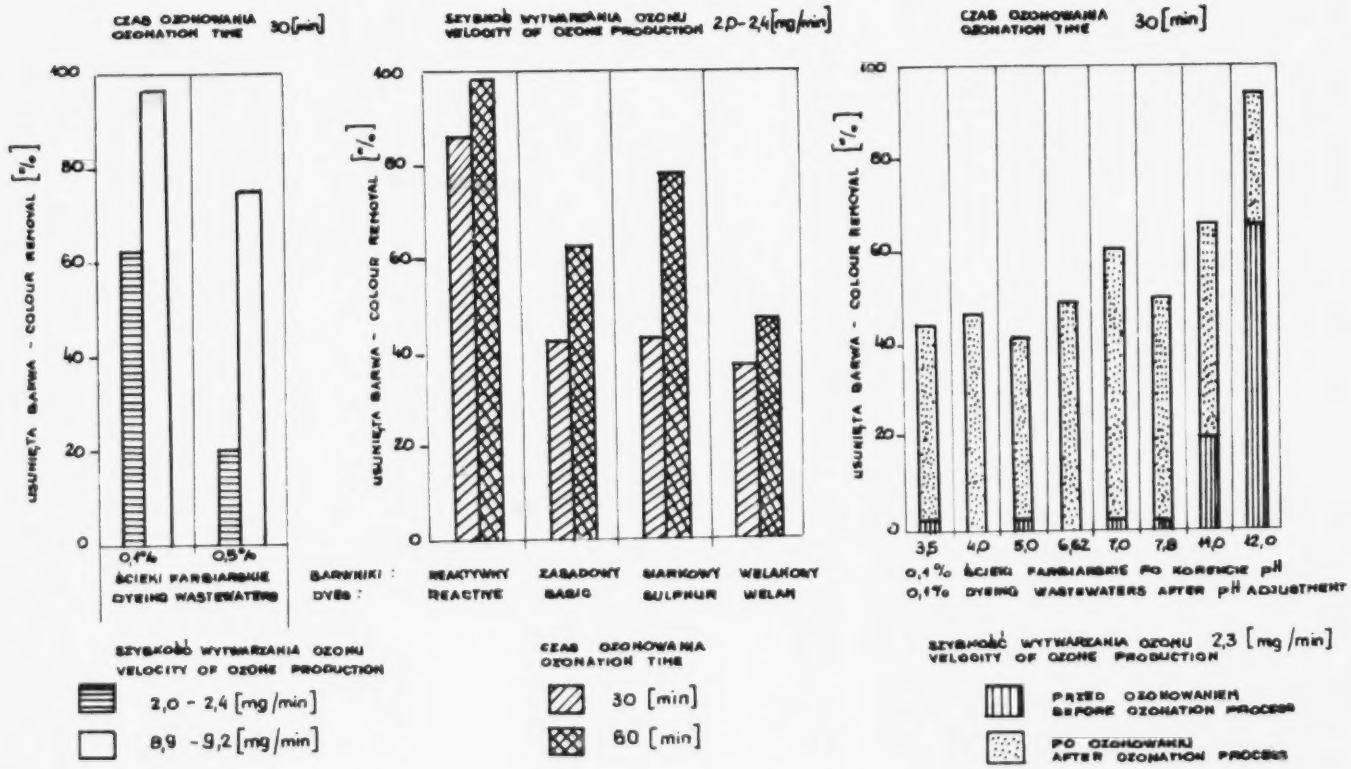
Rys 15. Efekty usunięcia barwy ze ścieków farbiarskich w zależności od czasu ozonowania.

Figure 15. Relationship between color removal and ozonation time in dyeing wastewaters ozonation process.



° 0.1% Ścieki farbiarskie
0.1% Dyeing wastewaters
x 0.5% Ścieki farbiarskie
0.5% Dyeing wastewaters

Rys 16. Efekty usuniecia barwy ze sciekow farbiarskich w zaleznosci od zuzytej dawki ozonu.
Figure 16. Color removal by ozonation effect of ozone consumed.



Rys 17. Efekty usuniecia barwy w procesie ozonowania roznych substratow.
Figure 17. Color removal by ozonation of different tested materials.

effects, especially for 0.5 percent wastewater for which maximum 75 percent of color removal were achieved (Fig. 17). Figure 18 shows the relationship between the amount of O_3 feed and the color removed. Ozonization of water solutions of the individual dyes showed that reactive dye had the highest oxidizability (Fig. 17 and 19). The remaining three dyes, i.e., sulfur, basic and welan were removed during 30 minutes in identical degree. However, differences in their removal rate were observed after 60 minutes (Fig. 17). The index of ozone consumption for individual dye removal confirms high oxidizability of reactive dye. In the case of reactive dye, the O_3 consumed per unit of dye removed (0.14 to 0.33 mg of O_3/mg) is the lowest among four tested dyes (Table 7).

As a result of the ozonization process, changes take place in the molecular configuration of dyes with partial oxidation of the carbon atoms. The observed changes in spectrum UV-Vis confirm this fact.

It was observed that color decay in ozonization process was accompanied by weakening of spectral bands or their complete decay. The ozone influence could be seen the soonest and clearest in the reactive dye.

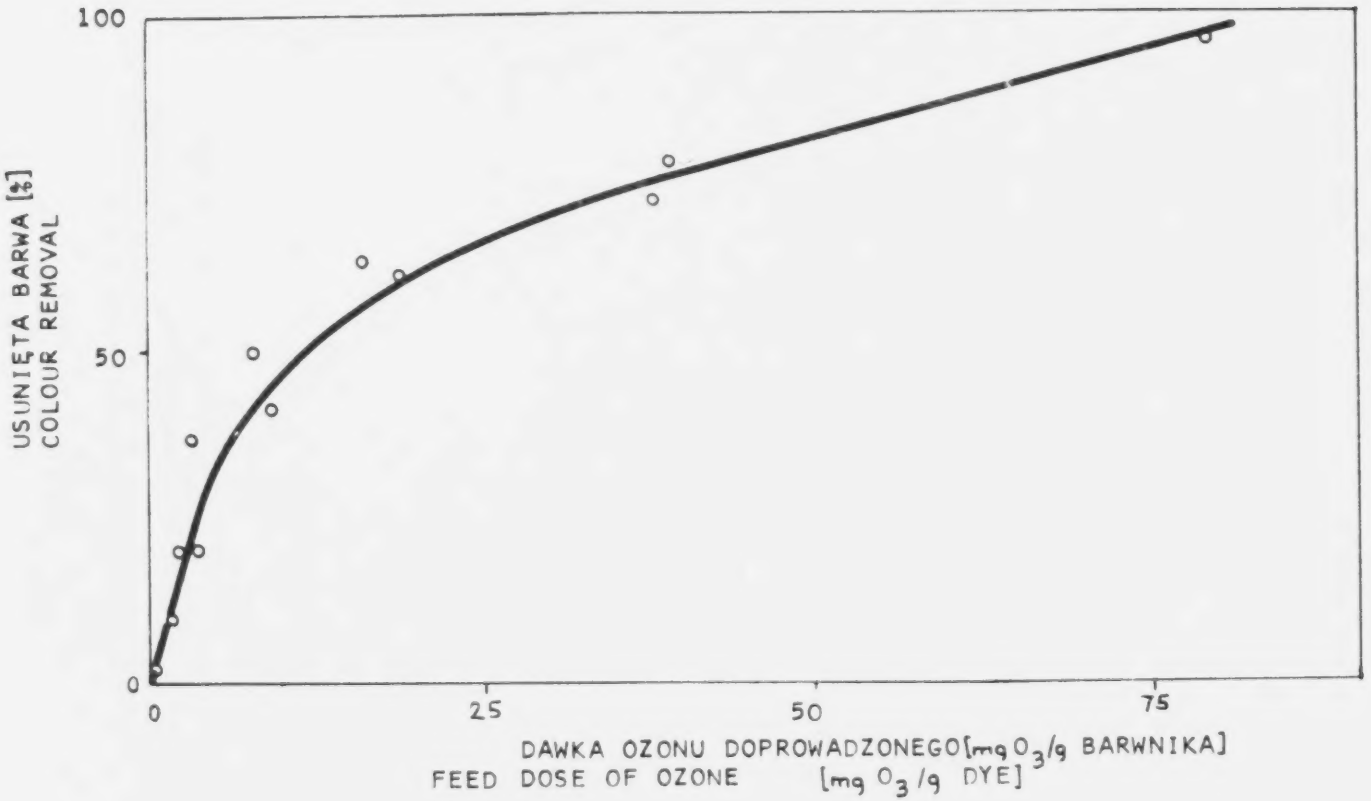
The best effects of color removal were obtained for the reactive dye. Color decay was accompanied by the decay of series of spectral bands in UV-Vis spectrum (Fig. 20).

The infrared spectrum obtained from reactive dye bath before ozonization and after 15 and 30 minutes of ozonization showed an adsorption at 1380 - 1375 cm^{-1}. As the ozonization proceeded there was a diminution of the wide band in "dactyloscopic area," and the appearance of a band in the range of 1460 - 1390 cm^{-1}, and weakening of the band in the range of 840 - 730 cm^{-1}. The peak at 870 cm^{-1} and adsorption above the frequency of 1400 cm^{-1} are due to the stretching vibration of carbonates (Fig. 21).

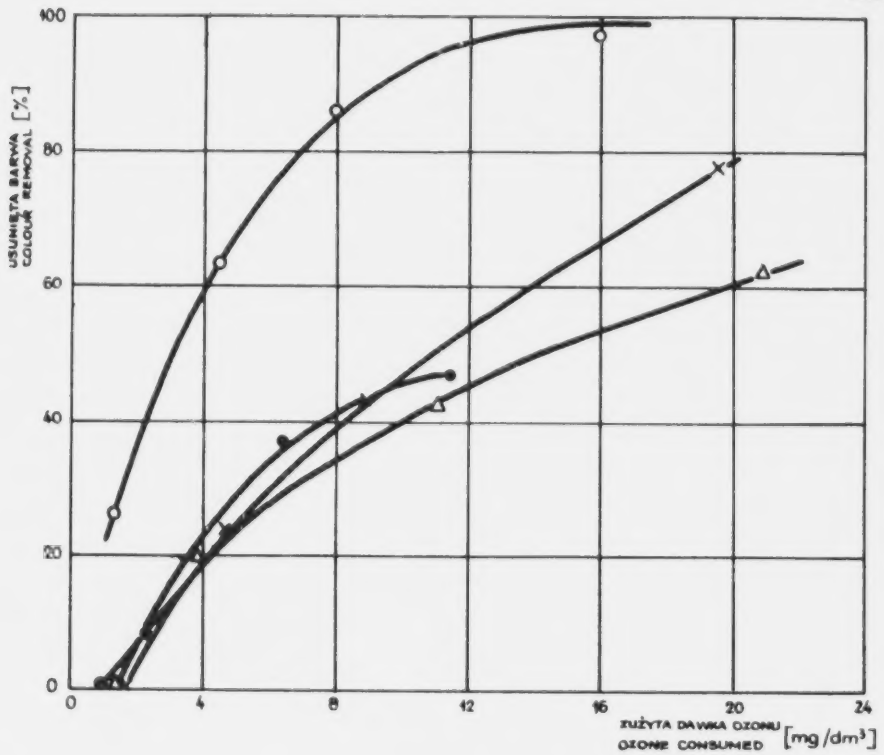
The influence of pH changes on ozonization effects was tested for 0.1 percent dyeing wastewater by 30 minutes contact with an ozone flow of 2.35 mg/min. Based on the obtained results, it can be stated that changing wastewater pH with the addition of H_2SO_4 or NaOH in the range of 3.5 to 9.0 does not affect the improvement of ozonization. Increase of pH up to 11 and 12 caused permanent, irreversible color removal of 20 percent and 56 percent, respectively.

Combining the alkalizing processes at pH 12 and ozonization process gave 94 percent of color removal. See Fig. 17 and 22. The positive effect of pH increase up to 12.45 by the addition of $Ca(OH)_2$ in ozonization process was observed by Reicherter and Sontheimer (3). These authors are of the opinion that pH increase leads towards quick decomposition of ozone and precipitation of partially oxidized organic substances.

However, in the case of our investigations, it seems that increased pH first causes hydrolysis of part of the dyes. This conclusion is according to results from tests on wastewater coagulation in Section 5.1. Oxidation takes place at lower pH values.



Rys 18. Zależność efektów usunięcia barwy od ilości doprowadzonego ozonu na jednostkę wagową barwnika.
Figure 18. Color removal by ozonation.



o Barwnki reaktywny - Reactive dye
Δ Barwnik zasadowy - Basic dye
X Barwnki siarkowy - Sulfur dye
● Barwnik welanowy - Welan dye

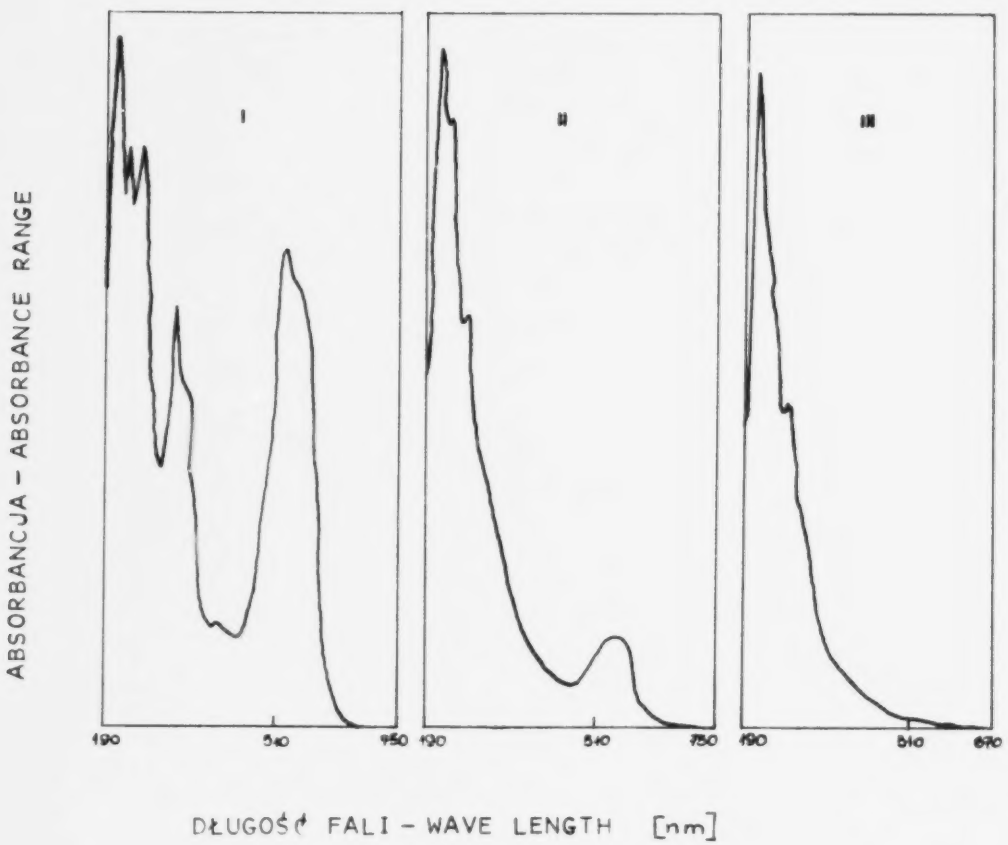
Rys 19. Efekty usunięcia barwy z 0.005% roztworów barwników w zależności od zużytej dawki ozonu.

Figure 19. Relationship between color removal and ozone consumed in 0.005% dyes solutions ozonation process.

TABLE 7. COD REMOVAL, AND OZONE CONSUMPTION INDEX IN OZONIZATION OF TESTED SUBSTRATES

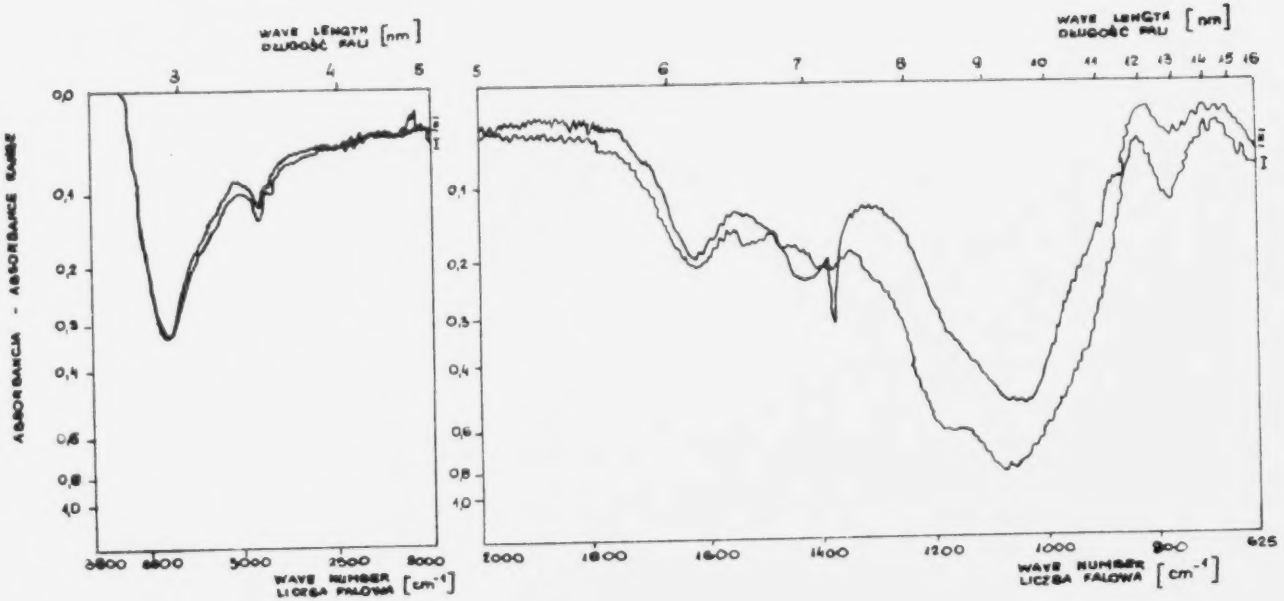
Substrate	Concentration %	COD removed from filtered[x] sample %		Ozone consumed for dye removed mg of O_3/mg	
		after 5 min	after 60 min	after 15 min	after 60 min
Dyeing wastewater	0.1	-	27.3	-	-
Dyeing wastewater	0.5	-	10.6[xx]	-	-
Water solutions of dyes					
reactive	0.005	56.2	11.0	0.14	0.33
basic	0.005	27.3	18.2	0.38	0.67
welan	0.005	-	4.8	0.58	0.48
sulfur	0.005	28.6	14.3	0.39	0.50

[x]filter paper
[xx]after 30 minutes



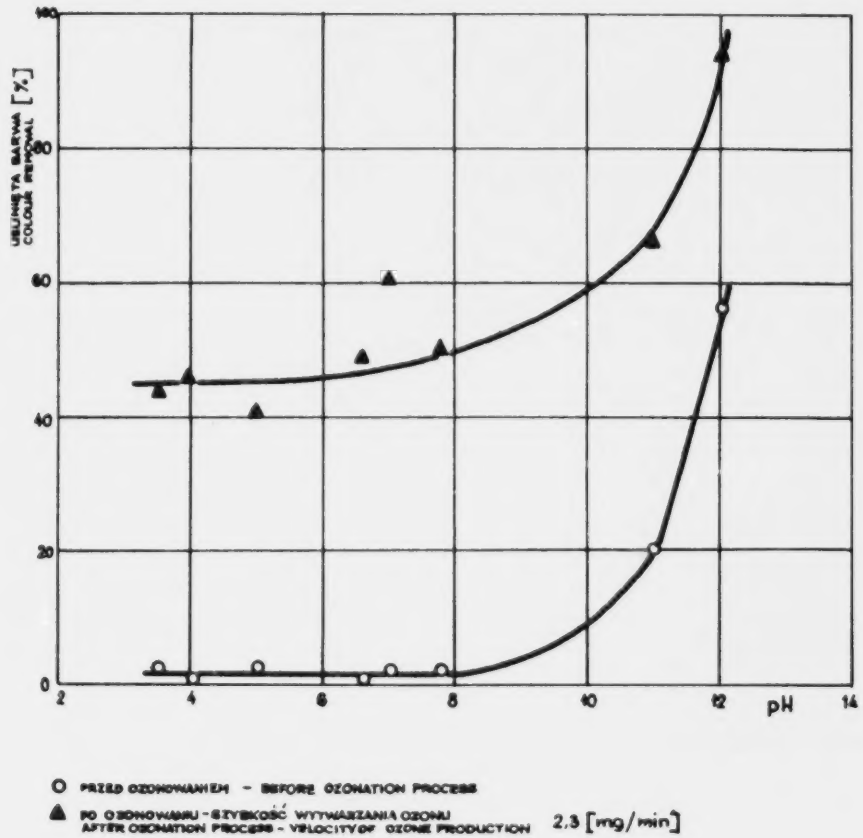
Rys 20. Widma wodnego roztworu barwnika reaktywnego.
I. Przed ozonowaniem
II. PO 15 minutach ozonowania
III. PO 30 minutach ozonowania

Figure 20. Spectra of the reactive dye water solution.
I. Untreated
II. After 15 minutes of ozonization
III. After 30 minutes ozonization



Rys 21. Widma ir wodnego roztworu barwnika reacktywnego,
I. Przed
II. PO 30 minutach ozonowania

Figure 21. IR-spectra of the reactive dye water solution.
I. Untreated
II. After 30 minutes ozonization



Rys 22. Wpływ zmian pH na efekt usunięcia barwy ze ścieków farbiarskich 0.1%.

Figure 22. Removal of color by ozonation - effect of pH variations 0.1% dyeing wastewaters.

The ozonization process did not cause high changes in COD. Maximum values of COD removed from the filtered sample were varied for various substrates. For example, they were: for 0.1 percent dyeing wastewater - 27.3 percent after 60 minutes of ozonization, and for 0.5 dyeing wastewater - 10.6 percent after 30 minutes of ozonization (Table 7). COD removal in the ozonization process depended on ozonization time. Generally shorter ozonization time and smaller ozone dose caused higher COD removal.

5.3 CHLORINATION

Methods and Range of Investigations

Chlorine and its compounds, on account of their oxidizing and disinfecting properties, are used in wastewater treatment not only for municipal but more and more frequently for industrial wastewaters (4). The investigations were carried out with laboratory equipment in static conditions using contact time with chlorine from 5 minutes to 24 hours, and a chlorine dose from 5 to 1000 mg/dm^3. See Fig. 23 for testing equipment. Samples catalyzed with ultraviolet color were irradiated by a quartz lamp at contact time from 2.5 to 15 minutes. Besides investigations were carried out on chlorination process preceded by CaO coagulation with and without neutralization. Chlorine was determined by the iodometric method. Wastewater treatment effects were defined on the basis of following indices: color, COD, BOD_5, anionic detergents, and pH. The investigations were carried out at room temperature equal to 20 °C.

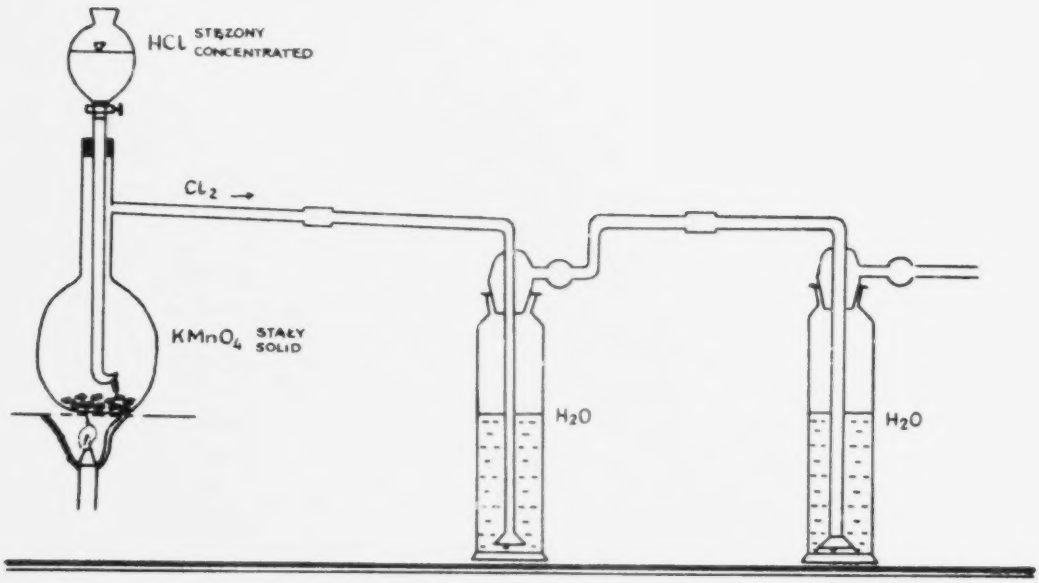
Discussion of the Investigations Results

As it had been anticipated as a result of oxidation process with chlorine, changes were observed in wastewater color as well as considerable percentage of color removal. Oxidation can either break the dye aromatic structure or change the functional groups.

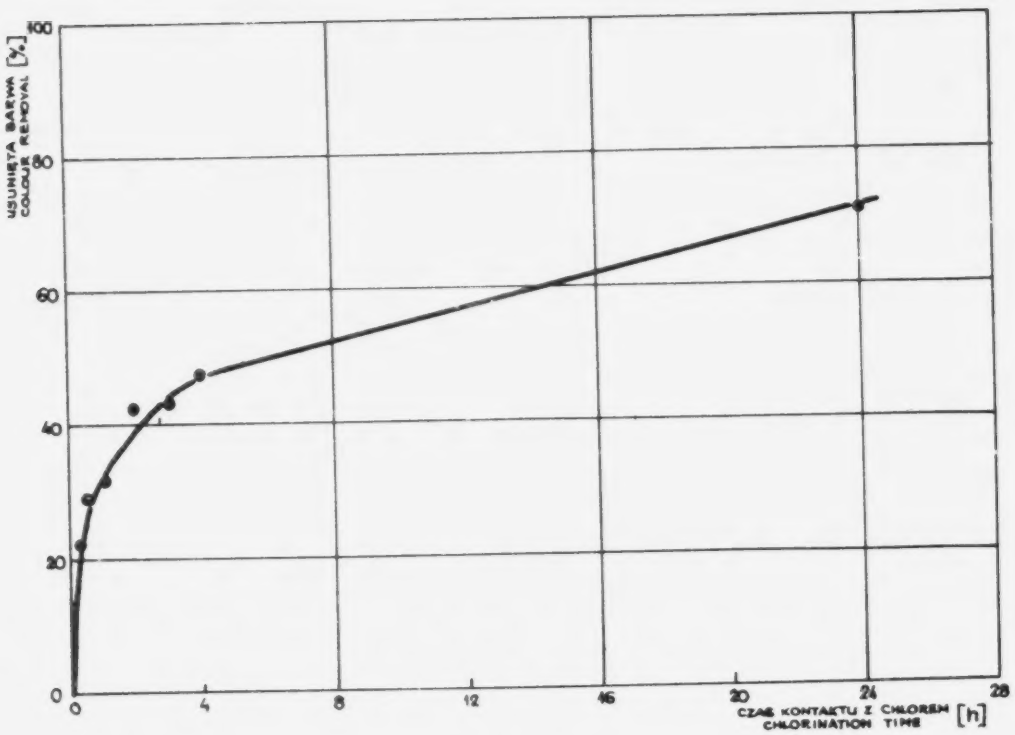
Technological investigations seem to indicate that the oxidation process changed the chromophoric group. These positions were confirmed by chromatographic analyses.

The oxidation process with use of chlorinated lime solution (Fig. 24) indicates a relatively low rate of oxidation. From the shape of the curve, it can be concluded that several oxidation reactions take place simultaneously at various rates. Chlorine consumption was proportional to the removed color (Fig. 25) independently of changes in chlorine dose from 5 to 1000 mg/dm^3 or of varying contact time from 15 min to 24 hrs.

Efficiency of oxidation with chlorine depends considerably on pH of the solution in which the reaction will take place. When chlorinated lime was used, the pH was distinctly alkaline in range from 9.42 to 10.34. When using chlorine water, pH was in acid range from 3.20 to 5.36.

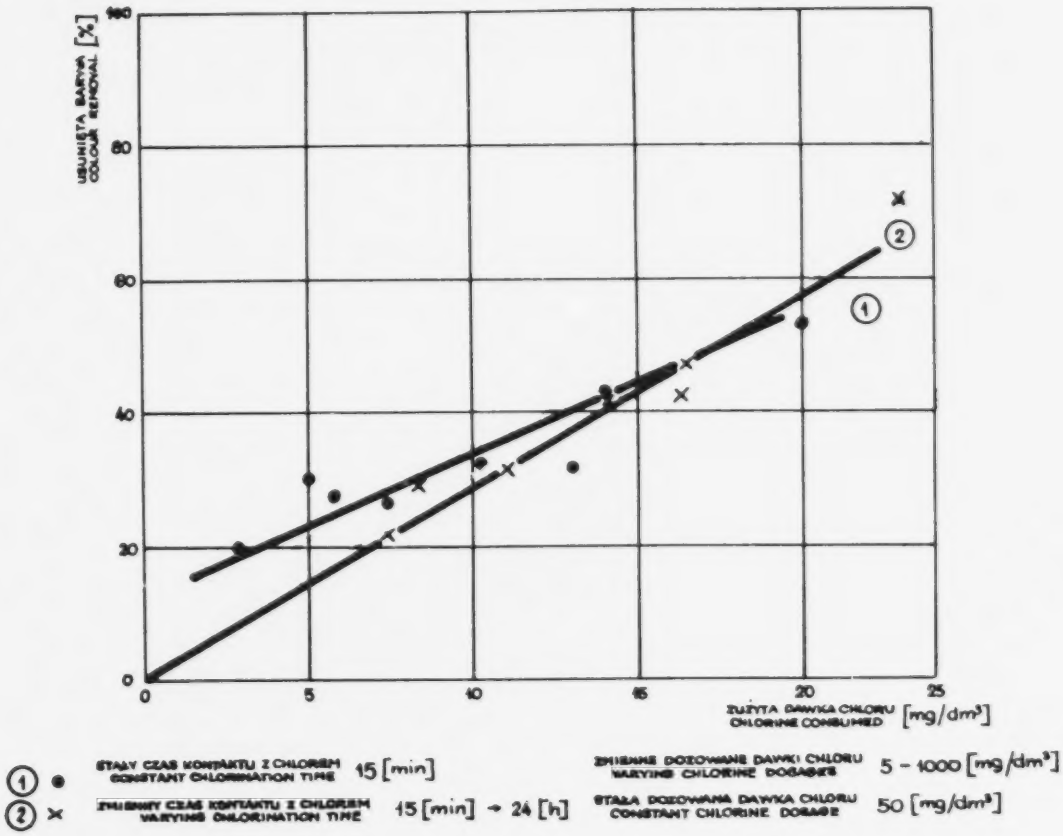


Rys 23. Aparatura do wytwarzania wody chlorowej.
Figure 23. Testing equipment for chlorine water production.



Rys 24. Zależność efektu usunięcia barwy ze ścieków farbiarskich 0.1% od czasu kontaktu z chlorem przy zastosowaniu roztworu wapna chlorowanego.

Figure 24. Relationship between color removal and chlorination time in 0.1% dyeing wastewaters chlorination process using lime chlorinated solution as an oxidizer.



Rys 25. Zależnośc efektów usunięcia barwy ze ścieków farbiarskich 0.1% od zuzytej dawki chloru przy zastosowaniu roztworu wapna chlorowanego.

Figure 25. Relationship between color removal and chlorine consumed in 0.1% dyeing wastewaters chlorination process - using lime chlorinated solution as an oxidizer.

When using chlorine water, considerably higher reaction rates were achieved. With a very small dose of chlorine in the range from 20 to 50 mg/dm^3 and a contact time of 15 minutes, the decoloration process was practically finished. The comparison between color removal and chlorine consumed using chlorinated lime and chlorine water is shown in Fig. 25 and 26. For example, when comparing color removal at a consumed amount of 20 mg/dm^3 of chlorine, there was only 53 percent color removal using chlorinated lime as contrasted to 99 percent using chlorine water.

The process of dyes oxidation with chlorine can be accelerated substantially with UV radiation (Fig. 27 and 27a).

Chlorine consumption in the reaction catalyzed with UV light was higher by about 15 percent than in the process without catalyst at the identical color removal effects. Higher chlorine consumption was caused probably by oxidation or chlorination of the remaining colorless pollutants contained in wastewater (detergents and assistants), and also by intensifying destruction of dyes molecules.

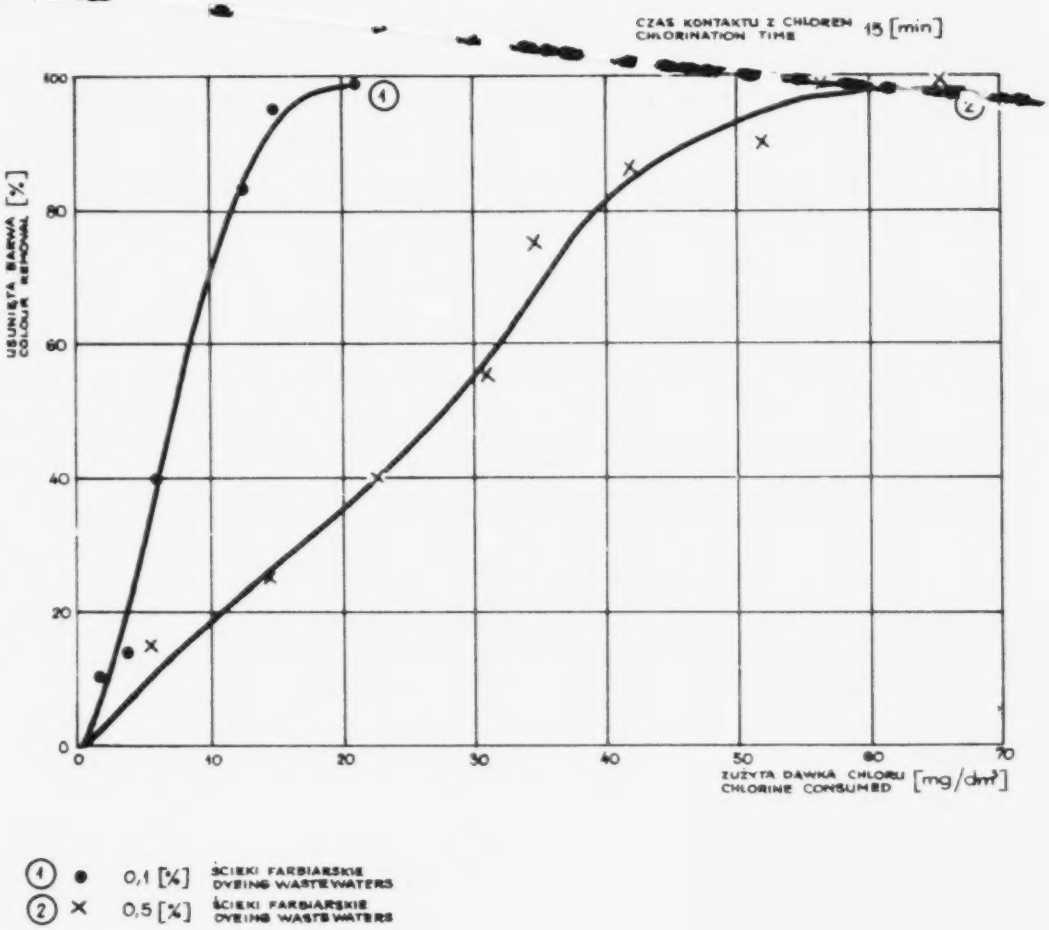
This thesis is also confirmed by the fact of higher chlorine consumption in the process using ultraviolet radiation at the use of a larger chlorine dose of 100 mg/dm^3 than at a dose of 50 mg/dm^3 of chlorine in spite of similar color removal.

When analyzing changes of other characteristic values, the "depth" of chlorination is seen very distinctly at the use of a bigger chlorine dose. After a 15 min chlorination period of dyeing wastewater previously irradiated, the following effects were obtained:

Removal effects	Chlorine dose	
	50 mg/dm^3	100 mg/dm^3
COD	30%	32%
BOD_5	50%	78%
Detergents	8%	55%

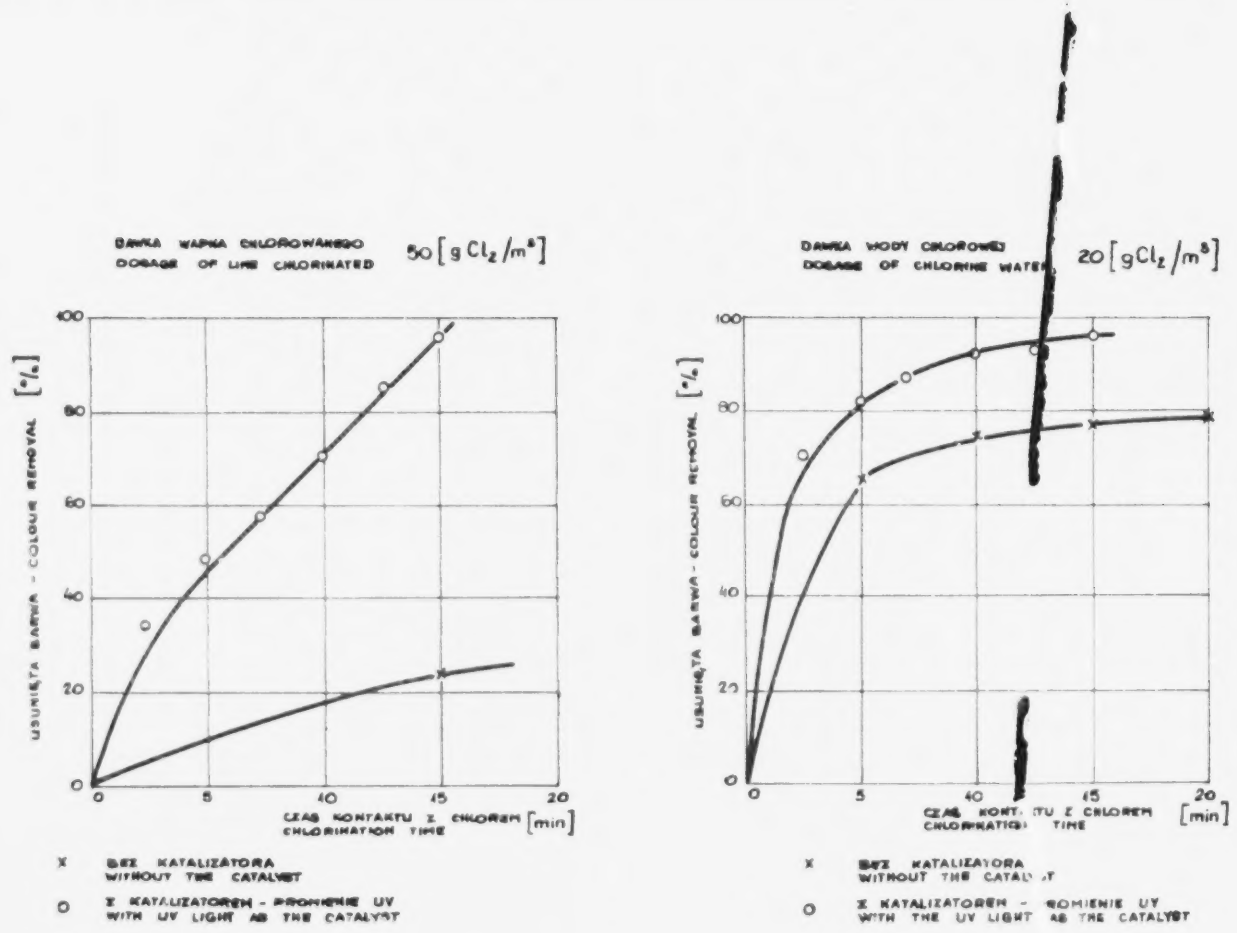
Another phenomenon worthy of noticing was that using chlorinated lime without UV radiation catalysis, after 24 hours less color removal was obtained than in catalyzed chlorination process after 15 minutes, but higher BOD_5 removals were achieved reaching 85 percent and detergents equal to 57 percent. The very small COD removal is surprising, being within the limit of determination error.

Since the chlorination of wastewater with chlorine water gave good color removal in 15 minutes of contact time, a comparison was carried out to determine the influence of UV light for the mentioned period of time but for various chlorine doses. For the chlorination process without catalysis, the



Rys 26. Zależność efektów usunięcia barwy ze ścieków farbiarskich od zuzytej dawki chloru przy zastosowaniu wody chlorowej.

Figure 26. Relationship between color removal and chlorine consumed in dyeing wastewaters chlorination process using chlorine water as an oxidizer.


DAWKA WAPNA CHLOROWANEGO 50 [g Cl₂/m³]
DOSAGE OF LIME CHLORINATED
USUNIĘTA BARWA - COLOUR REMOVAL [%]
CZAS KONTAKTU Z CHLOREM [min]
CHLORINATION TIME
X BEZ KATALIZATORA
WITHOUT THE CATALYST
O Z KATALIZATOREM - PROMIENIE UV
WITH UV LIGHT AS THE CATALYST
DAWKA WODY CHLOROWEJ 20 [g Cl₂/m³]
DOSAGE OF CHLORINE WATER
USUNIĘTA BARWA - COLOUR REMOVAL [%]
CZAS KONTAKTU Z CHLOREM [min]
CHLORINATION TIME
X BEZ KATALIZATORA
WITHOUT THE CATALYST
O Z KATALIZATOREM - PROMIENIE UV
WITH THE UV LIGHT AS THE CATALYST

Rys 27. Porównanie efektów usunięcia barwy z katalizą UV i bez dla 0.1% ścieków farbiarskich.
Figure 27. Color removal by chlorination of 0.1% dyeing wastewaters - effect of UV light as catalyst.

dose of 50 mg of Cl_2/dm^3 was used while for the catalyzed process - 20 mg of Cl_2/dm^3.

From the comparison shown below, it can be noted that when the chlorination was catalyzed, the COD was reduced by 24 percent in comparison with no COD removal in the not catalyzed process.

CHLORINATION WITH CHLORINE WATER

Dose, mg/dm^3	20	50
Catalysis	UV	without
Reaction time, min	15	15
Cl_2 consumption, %	79	62
pH	3.5	3.5
Removal effects, % of		
- color	97	97
- COD	24	0
- BOD_5	66	77
- Detergents	60	55

In the chlorination process, a considerable decrease of pH takes place down to the value of about 3.2. Wastewater neutralization after chlorination, with lime, does not cause any changes in the color removal.

High doses of chlorine gave effective color removal from 0.5 percent dyeing wastewater (Fig. 26). For the higher doses of 100 and 120 mg/dm^3, practically complete color removal was obtained reaching 99 percent. Lower consumption of chlorine, as it could result from the increase of dyeing wastewater concentration, is characteristic. At chlorine consumption in the range from 54 to 77 percent, the chlorine use was only 3.5 times higher than for wastewater 5 times more concentrated.

Conduction of the effective wastewater decolorization by chlorination requires a certain amount of excessive free chlorine present in wastewater. When using a constant chlorine dose of 50 mg/dm^3 and a changeable contact time, only 83 percent of color removal was possible. Such effect was obtained after 30 min contact and extending this time had no influence on decolorization and concentration of the remaining chlorine at the level of 10 mg/dm^3. Therefore, a stability point of oxidation reaction can be considered.

When conducting the chlorination process on 0.5 percent dyeing wastewater, UV radiation neither accelerated nor increased color removal, contrary to the results obtained for 0.1 percent wastewater.

This phenomenon was probably connected with a too low concentration of free radicals generated from the ultraviolet light in relation to a relatively high concentration of pollutants contained in wastewater. At the same time, the concentration of these radicals was being decreased by a strong inhibitor of radical reaction, namely oxygen, which was generated in the decomposition reaction

of hypochlorous acid. The decomposition of HOCl is accelerated considerably by UV radiation.

When conducting the chlorination process on lime coagulated wastewater, the chlorination process causes further decrease of dyes concentration in the wastewater. See Fig. 28. However, the earlier decrease of wastewater pH to the value close to pH = 7 is very important. At wastewater saturation with CO_2, the precipitation of calcium carbonate takes place causing certain additional reduction of color (Fig. 28).

At the same time one can suppose that wastewater chlorination at pH value close to neutral causes higher use of chlorine for dyes structure decomposition, while in the case of alkaline reaction part of the chlorine reacts with calcium ions, and the general rate of the chlorine reaction with dyes is distinctly decelerated.

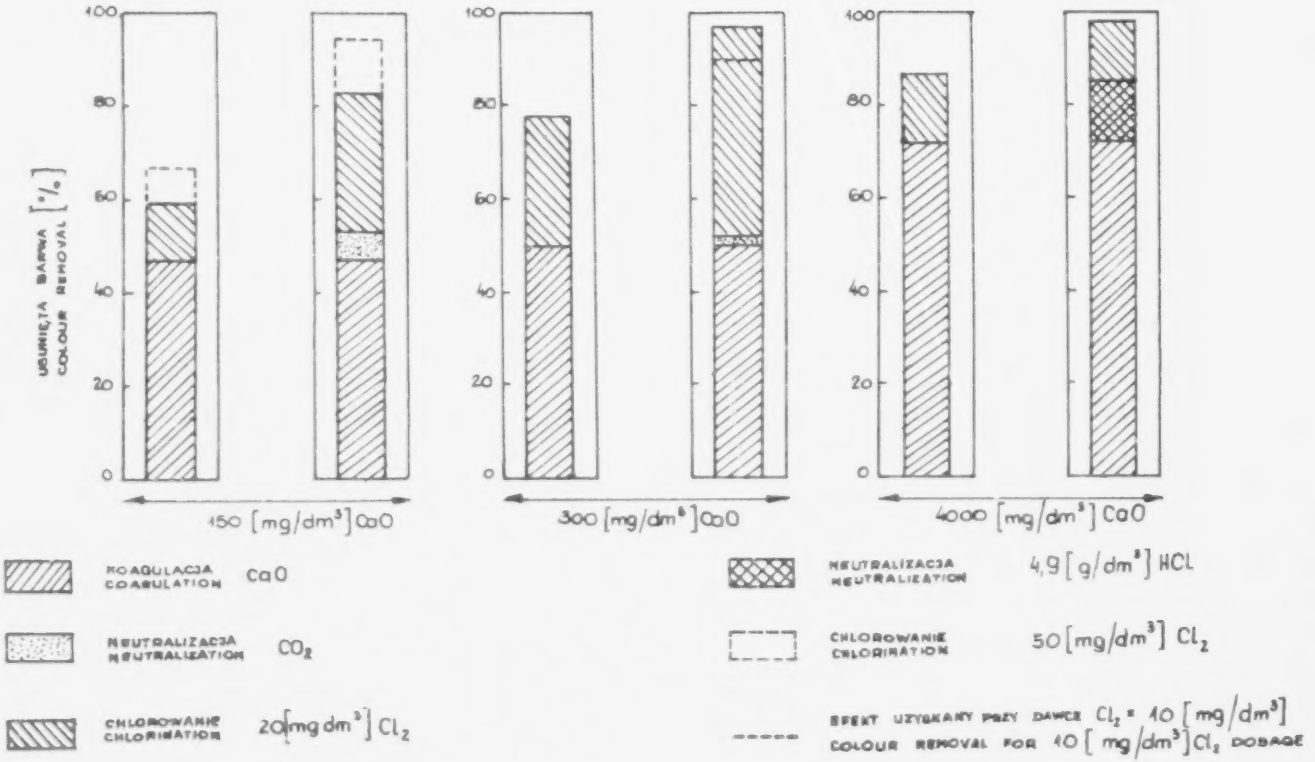
Color removal obtained jointly in a composite treatment process, which consists of coagulation, neutralization, and chlorination, was higher than these obtained in the individual processes. However, use of the above mentioned composite process only for color removal from wastewater seems technically unjustified. But in the case of wastewater treatment, the neutralization of wastewater is necessary before their discharge into surface water. Then the coagulation process with CaO and neutralization will be reasonable. Similarly, if for sanitary reasons wastewater chlorination will be required as the last stage of wastewater treatment, then the whole described technological train is fully justified.

During wastewater treatment process containing - coagulation - neutralization - chlorination - clarification - certain COD removal also takes place. However, the removal effects are not too high and reach about 20 percent.

Chlorination process with relatively small doses of chlorine, but with a long contact time caused color removal and change of color. Visually red color turns to orange and finally to yellow (straw-yellow). During chromatographic analysis with blotting paper, the distinct trace concentration of dyeing substances was observed in wastewater visually almost decolored in chlorination process.

From an analyzed sample, a zone of 188 mm^2 strongly colored blue-purple was obtained using an anion exchange blotting paper. After the chlorination process, wastewater decolored to a maximum gave on the same type of blotting paper a weakly colored light yellow zone of 95 mm^2. These light colors may be the remaining original components or products of chemical changes of different chromosome groups.

Changes in dyes structure caused by chlorination of 0.1 percent solution of dyeing wastewater were also recorded in a thin-layered analysis. Chromatographic thin layered analyses were carried out with silica gel in a solvent of: pyridine:ammonia:water (1.3:1:1). The obtained results for untreated wastewater were the following:



Rys 28. Usunięcie barwy ze ścieków farbiarskich 0.1% w procesach koagulaji neutralizacji i chlorowania.
Figure 28. Color removal in 0.1% dyeing wastewaters treatment process by coagulation, neutralization and chlorination.

Rf. 100	
	99 purple band
	95 orange band
	89 purple band
	87 yellow fluorescence in UV light
	76 purple band
	74 red-purple band
	71 violet-purple band
	68 red band

After chlorination, wastewaters decolorized to weak yellow tint showed distinct green-yellow fluorescence in ultraviolet light. In chromatograms the band colors were considerably less intensive, while in ultraviolet light series of bands of distinct fluorescence appeared:

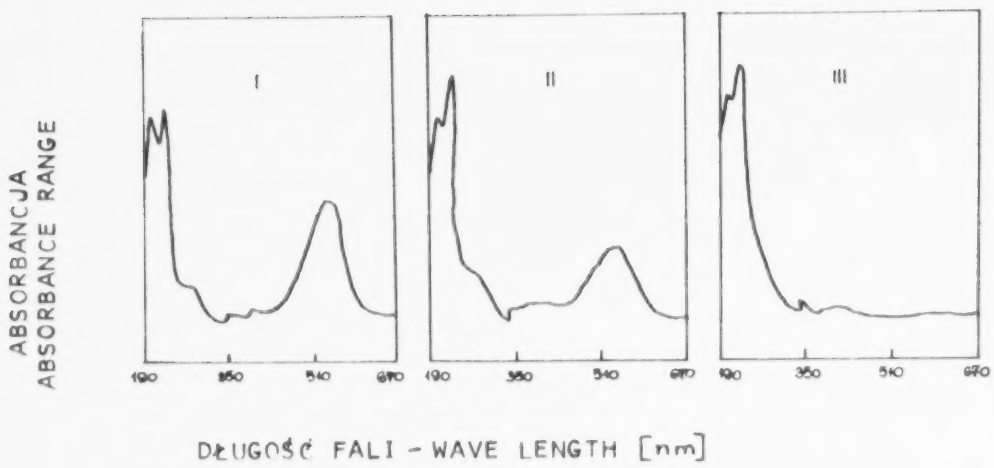
Rf. 100	Band color	Fluorescence
99		yellow
95		"
92		blue
87		yellow
83	orange	-
82	weak purple	-
80	-	violet
79	red	-
76	-	yellow
74	brown-yellow	-
71	-	yellow

In order to achieve full information of the character of reactions that take place, spectrographic analyses were done in the ultraviolet and visible ranges as well as in infrared range.

The UV-Vis spectra for 0.1 percnet wastewater undergoing chlorination process during 15 minutes with the use of chlorine water of chlorine concentration from 2-50 mg/dm^3 show gradual decreasing of the band intensity in a visible range as the color decayed. When the dose of chlorine was 30 mg/dm^3, the color of the sample changed from red to light yellow, and the spectra show complete decay of the band in a visible range.

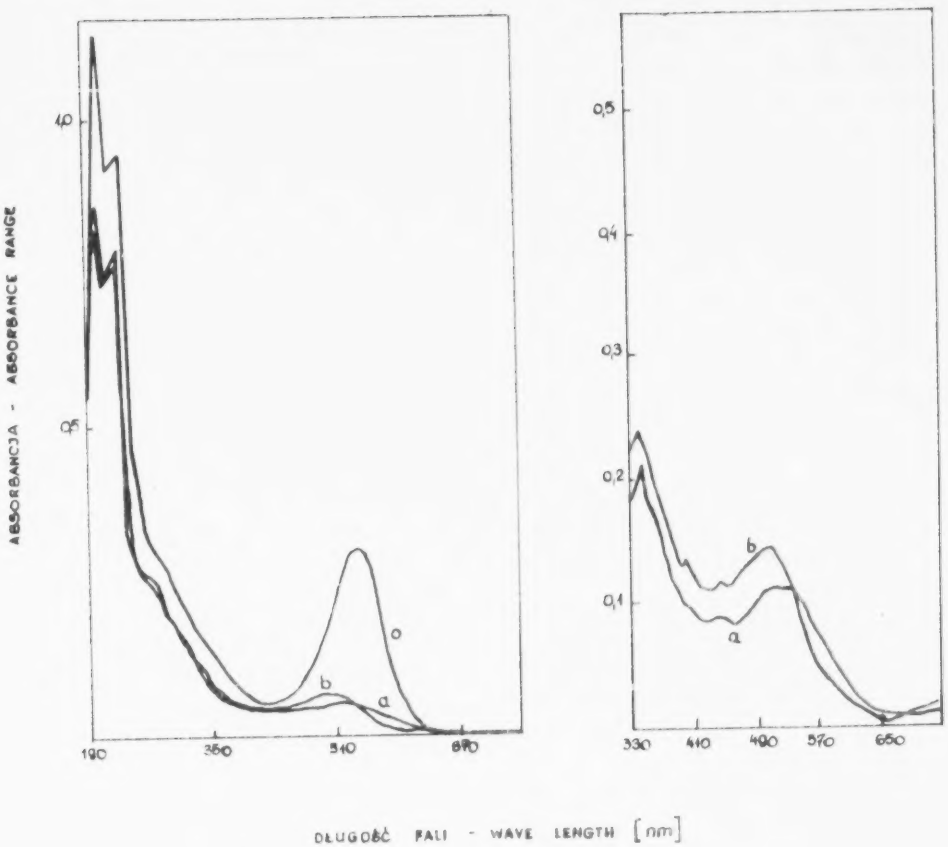
Examples of spectra that were obtained after chlorination at chlorine concentrations of 2, 10 and 50 mg/dm^3 are shown in Fig. 29. In UV range a reduction of 286 nm and 206 nm bands was observed, but a strong absorption at 235 nm indicates an absorption of remaining aromatic structures. Under influence of 20 mg/dm^3 dose of chlorine and various exposition periods, one could follow the changes occurring within the exposition period corresponding to color transformation from red to orange. Considerable reduction in color intensity that was observed after 5 minutes of chlorination was maintained at the same level during subsequent reaction run for 180 minutes (Fig. 30).

The spectra in Fig. 30 shows a hypochromic effect in the visible range band as well as hypsochromic shift that may be a result of influence of more ionized reaction medium or by substitution.



Rys 29. Widma 0.1% ścieków farbiarskich po 15 minutach chlorowania dawkami. I. 2 mg/dm^3 chloru
II. 10 mg/dm^3 chloru
III. 50 mg/dm^3 chloru

Figure 29. Spectra of 0.1% dyeing wastewaters after 15 minutes of chlorination applying. I. 2 mg/dm^3 of chlorine
II. 10 mg/dm^3 of chlorine
III. 50 mg/dm^3 of chlorine



Rys 30. Widma 0.1% ścieków farbiarskich.
0 - przed i po chlorowaniu przez
a - 5 minut - dawka chloru 20 mg/dm^3
b - 180 minut dawka chloru 20 mg/dm^3

Figure 30. Spectra of 0.1% dyeing wastewaters.
0 - untreated
a - after 5 minutes chlorination applying 20 mg/dm^3
b - 180 minutes chlorination applying 20 mg/dm^3

The spectra recorded from 0.5 percent wastewater chlorinated with a chlorine dose of 50 mg/dm^3 showed similarly a hypochromic effect in the band of visible range increasing with chlorine action, and also hypsochromic effect. Moreover, a transitional absorption band appeared at about 370 nm, declining when the orange color was being transformed to yellow (Fig. 31).

In IR spectra obtained after 50, 75, and 100 minute chlorination, the following changes appeared: decay of nitrile band, considerable reduction in 3400 cm^{-1} band intensity, and an almost complete decay of alkane bands in the range of 2975 - 2840 cm^{-1}. A different new band appeared with increasing intensity according to the time of chlorination (Fig. 32). The maximum of the band is in the range of 3200 - 3100 cm^{-1}. The changes suggest a shift of alkane bands influenced by arising electronegative groups. This may be chlorine in the form of chlorinated derivative, or oxygen connected with carbon adjacent to alkane group. However, the shift is greater that those published in the literature for such effects. Since decreasing intensity of 3400 cm^{-1} band is observed, one can assume that there are reactions occurring at the same time within amine groups.

The kind of the reaction is undeterminable using the spectrum. One can only pay attention to occurrence of bands in the absorption range of oximes. At lower frequencies a decay of the 1580 - 1570 cm^{-1} band is observed, a new broad band appears with maximum at 1665 cm^{-1}, which is likely to be related to the structural elements: C = 0, C = N, N = 0.

Decay of the 1420 - 1410 and 870 cm^{-1} bands was observed. These bands are attributed to carbonate ions. As the chlorination period was prolonged, the intensity of the new 1400 cm^{-1} band increased and the band at 1380 cm^{-1} declined. In "finger print region" reduction of absorption in the band at 1100 - 1000 cm^{-1} occurred, but no significant changes are found in the band of 1200 - 1100 cm^{-1}.

5.4 BROMINATION

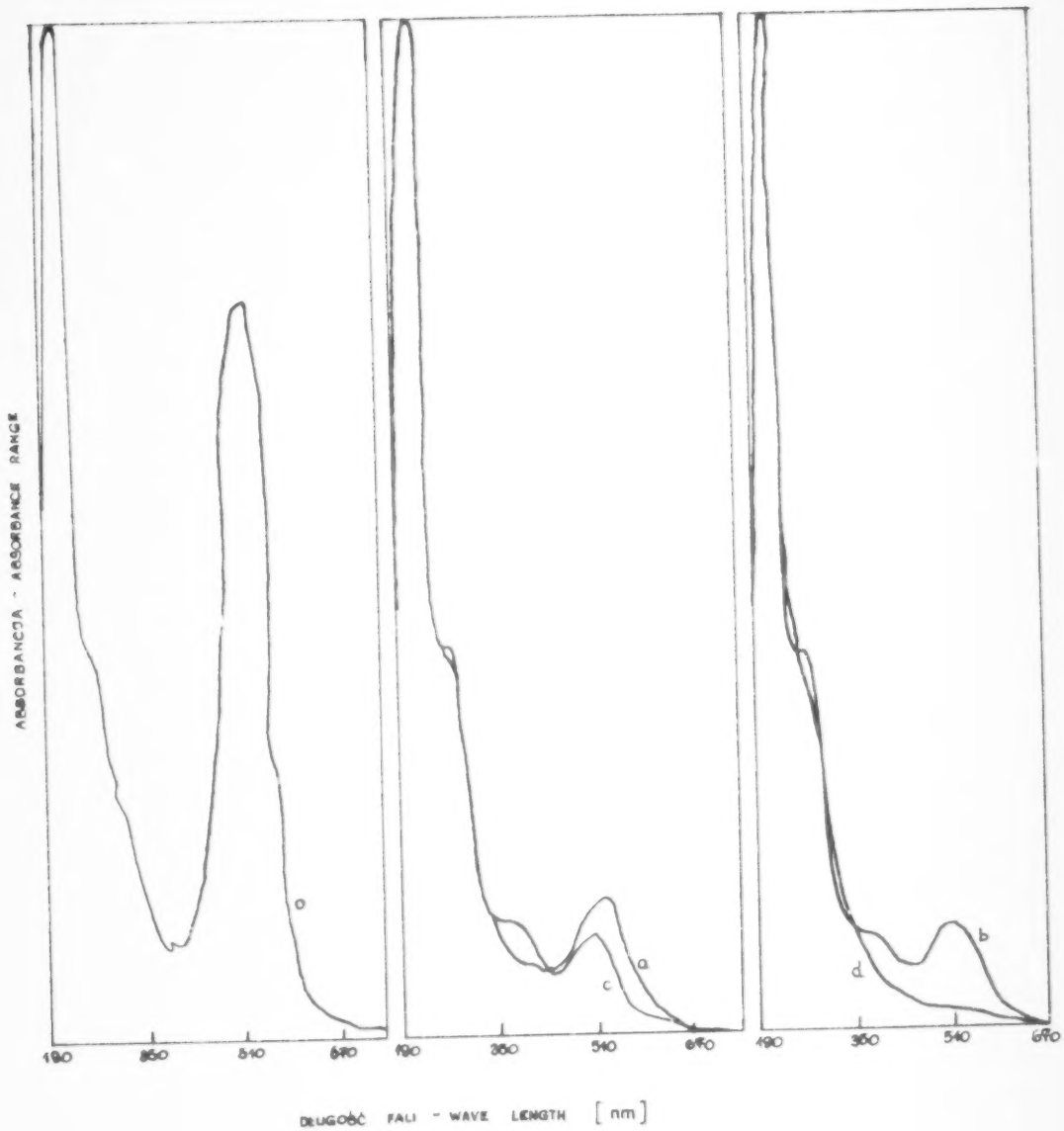
Methods and Range of Investigations

Bromine as an oxidant has been used for decolorization of wastewater generated in pharmaceutical industry. According to the literature, bromine was not used for textile wastewater treatment.

In the framework of presently reported work, the bromination process was carried out by dosage of bromine water into wastewater containing 0.1 and 0.5 percent solutions of dyeing wastewater. Various contact times from 1 minute to 24 hours of various various bromine doses from 5 to 200 mg/dm^{3}3 were used.

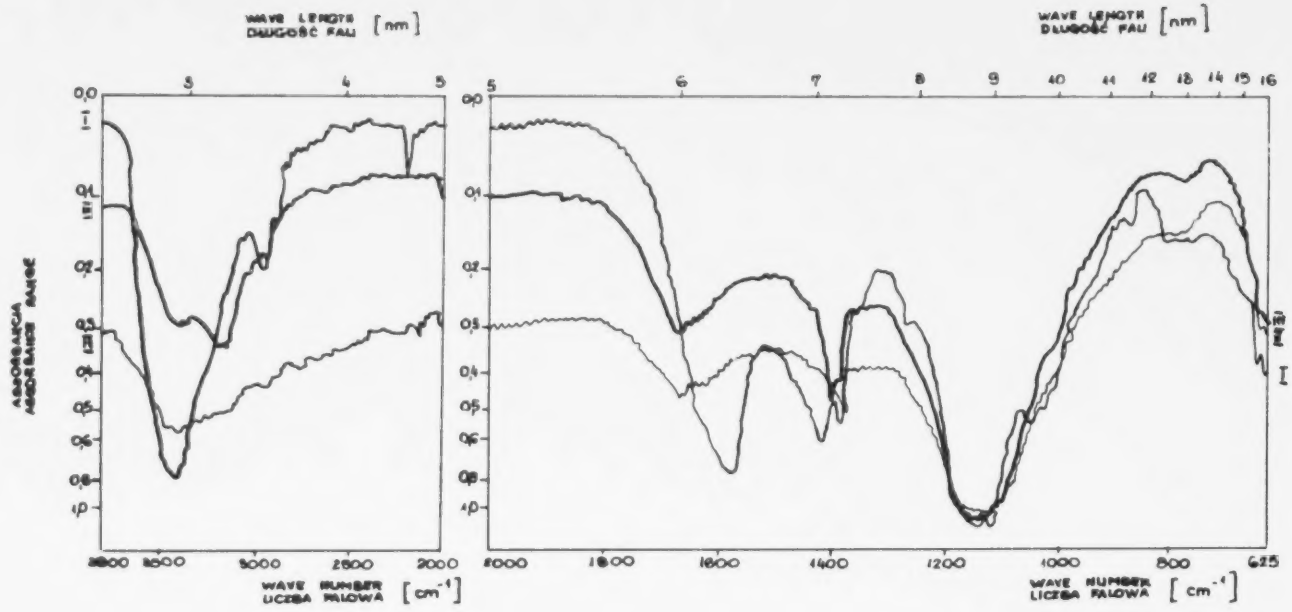
Bromine water used for the investigations was prepared by dissolving bromine in water, so that it contained from 12.5 to 16.5 g/dm^3 of free Br_2.

The laboratory investigations were carried on at a temperature of 20 °C and with continuous sample mixing. Remaining bromine was determined by iodometric method. Wastewater treatment effects were defined on the basis of such indices as color, COD, BOD_5, radioactive detergents and pH.



Rys 31. Widma 0.5% ścieków farbiarskich. O - przed chlorowaniem; a, b, c - po chlorowaniu dawką 50 mg/dm^3 do zmiany zabarwienia na pomarańczowe; d - j.w. do zabarwienia żółtego.

Figure 31. Spectra of 0.5% dyeing wastewaters. O - untreated and after chlorination applying 50 mg/dm^3 of chlorine until changing of purple hue to a, b, c, - orange, d - yellow.



Rys 32. Widma-IR 0.5% ścieków farbiarskich przed (I) oraz po 50 min (II) i 100 min (III) oddzialywania chloru.

Figure 32. IR-spectra of 0.5% dyeing wastewaters. I - untreated
II - after 50 minutes of chlorination
III - after 100 minutes of chlorination

Discussion of the Investigations Results

Color removal from dyeing wastewater by the bromination process occurs at a high rate. Decolorization takes place almost immediately after mixing of wastewater sample with bromine water.

When the testing of the bromination effect at a dose of 40 mg/dm^3 of Br_2 for 0.1 percent solution of dyeing wastewater with contact time of 1, 3, 5, 10, 15, 30, 60, 120, 180 minutes and 24 hours, the permanent effect of color removal obtained is shown in Fig. 33.

However at the same time, the level of bromine use increased as contact time increased. For 0.1 percent solution of dyeing wastewater, the level of bromine use changed from 51 to 74 percent. For 0.5 percent solution of dyeing wastewater, this level changed from 67 to 98 percent. The increasing bromine use together with contact time was caused probably by bromine evaporation to environment during sample mixing, and with partial bromine consumption in other reactions running at a lower rate or causing deeper destruction of dyes.

This thesis was partially confirmed by the results of COD, BOD_5, and anionic detergents for 0.1 percent solution of wastewater at a contact time of 1 and 30 minutes and for a constant bromine dose of 40 mg/dm^3 of Br_2.

REMOVAL EFFECT

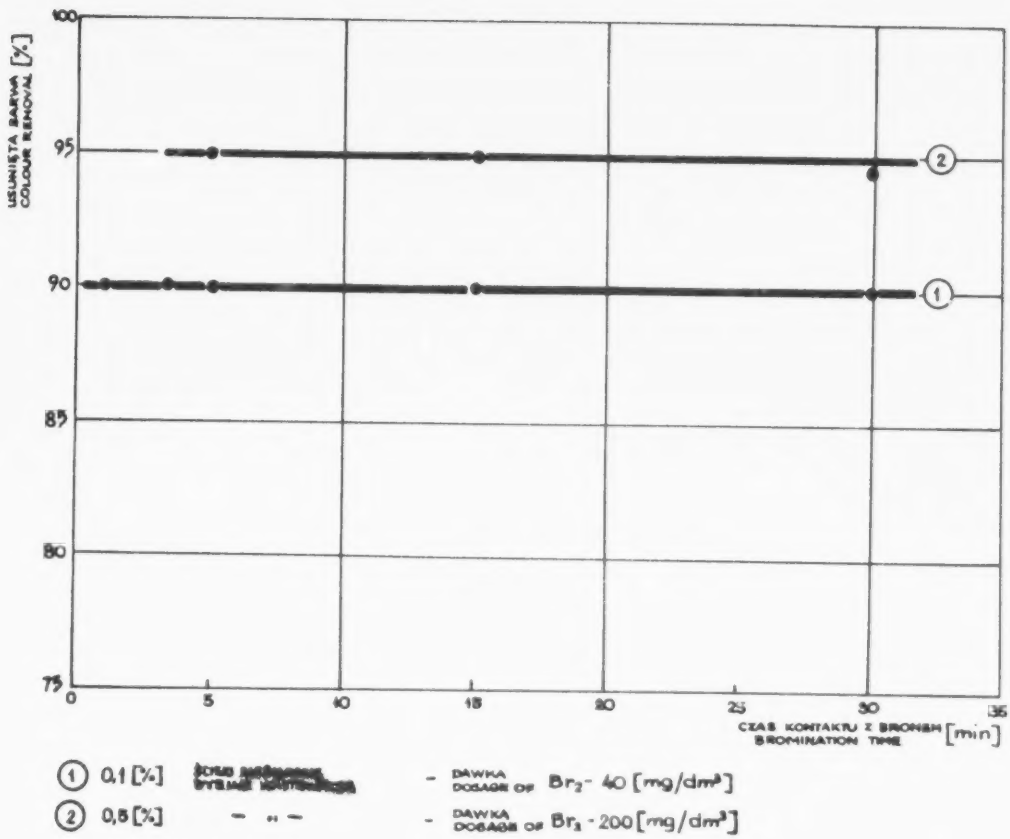
	1 Min.	30 Min.
COD	5.3%	15.9%
BOD_5	12.9%	17.0%
Detergents	60.0%	67.0%

The degree of color removal fundamentally depended on the appropriate dose of bromine. At the same time the bromine use level decreases as the provided dose of bromine increases for the given contact time.

When using a constant reaction time of 5 minutes in case of 0.1 percent solution of dyeing wastewater and various doses of bromine ranging from 5 to 200 mg/dm^3 of Br_2, the bromine use level obtained was in the range from 100 to 24 percent. At the same time as the bromine dose increased, the color removal effect was increasing, too, in a given case, from 20 to 100 percent (Fig. 34).

When using a constant reaction time of 5 minutes in case of 0.5 percent solution of dyeing wastewater and various doses of bromine in the range from 5 to 500 mg/dm^3 of Br_2, the bromine used level obtained was in the range from 100 to 49 percent. As the bromine dose increased, the color removal was also increasing in the range from 11 to 95 percent (Fig. 34).

The maximum value of color removal effect was obtained at the dose of 200 mg/dm^3 of Br_2

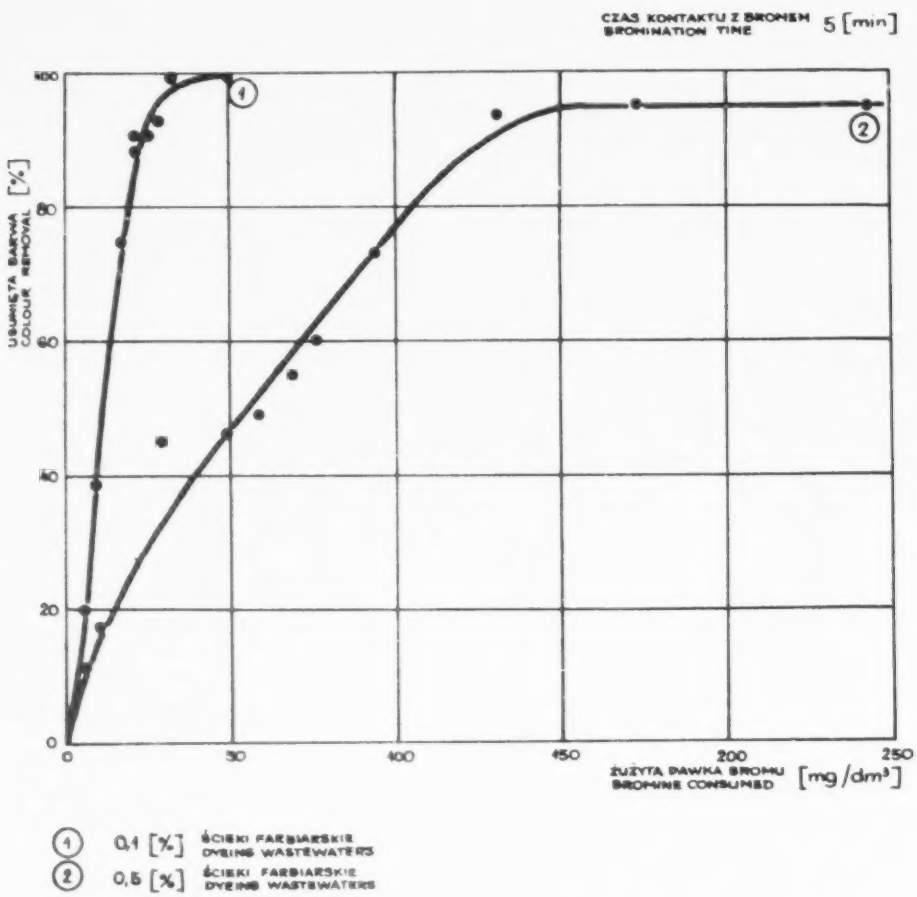


① 0,1 [%] - DAWKA Br_2 - 40 [mg/dm³]

② 0,5 [%] - " - - DAWKA Br_2 - 200 [mg/dm³]

Rys 33. Zależność efektów usunięcia barwy ze ścieków farbiarskich od czasu kontaktu z bromem

Figure 33. Relationship between color removal and bromination time in dyeing wastewaters bromination process



Rys 34. Zależność efektów usunięcia barwy ze ścieków farbiarskich od zuzytej dawki bromu.

Figure 34. Relationship between color removal and bromine consumed in dyeing wastewaters bromination process.

During the investigations, the characteristic partial color removal of untreated wastewater was turning from red color through orange into yellow. These changes evidence transformations that take place in dyes chromophore groups.

The paper chromatography on anionic blotting paper showed a change of zone of strong blue-purple tint of a surface equal to 188 mm^2 into a zone of intensive yellow color of a surface area of 74 mm^2. In this zone a more condensed zone could be distinguished of a surface of 42 mm^2.

Changes in dyes structure resulting from their bromination were clearly visualized in thin-layer chromatographic analysis. As it was earlier reported, such analyses were carried out with silica gel in the composition: pyridine: ammonia:water in the proportions: 1.3:1:1.

A sample decolored with bromine water to orange tint showed yellow-green fluorescence in UV light, as shown below:

Rf. 100	Band color	Fluorescence
(97)	-	yellow
(91)	-	blue
89	orange-yellow	-
87	yellow	-
83	brown	-
80 (80)	brown	yellow
(78)	-	yellow
76	brown	-
(74)	-	yellow

A sample decolored at a maximum degree to pale-yellow tint showed green fluorescence, and the appropriate data were:

Rf. 100	Band color	Fluorescence
(99)	-	blue
(93)	-	yellow
91	orange-brown	-
(89)	-	yellow
87	brown	-
84	brown	-
78	brown	-

( )Fluorescence spots

The decay of many chromatographic bands in comparison to the chromatogram of untreated wastewater solution given in chapter 5.3 is very characteristic. Many orange-yellow bands appeared and particularly brown ones. These are probably due to dyes in solution, namely welan or sulfur dye. The found brown bands would indicate generation of different chromophore groups. The arising of many fluorescence bands results probably from changes of function groups after oxidation or substitution with bromine.

When analyzing spectra after wastewater oxidation with bromine water in IR band, the changes were similar to chlorination. Slight variations were only observed between chlorinated and brominated wastewater spectra within the "fingerprint range."

UV-Vis spectra show the following changes: after bromination process the absorption band shifted from 540 nm to 510-500 nm. Hypsochromic shift was accompanied by considerable hypochromic effect.

New bands were produced at the same time at 440 nm and 395 nm (Fig. 35). Sample color changed to orange, orange-yellow and yellow. The spectrum of pale yellow sample showed decay of bands in visible range. In UV-range hypsochromic effects occurred as well as the increased absorption in the shortest wave length band (Fig. 36).

Both in chlorination and bromination processes, the changes in observed spectra indicated changes in functional groups determining a type of chromophoring system and functions of auxochromes. Strong absorption in the ultrabiolet range and negligible spectral changes in this range indicate conservation of aromatic structures in wastewaters after color removal.

5.5 ADSORPTION

Methods and Investigations Range

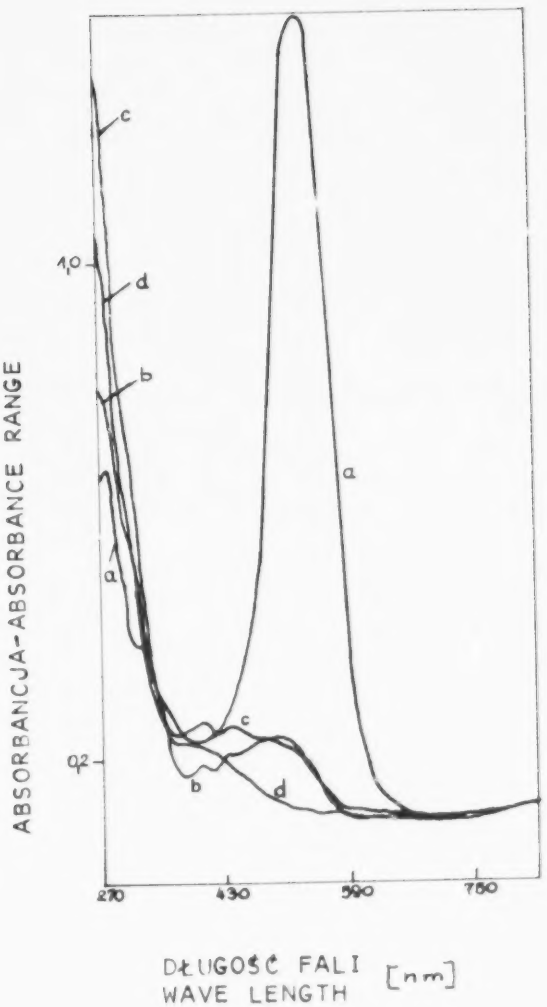
The investigations were carried out with the use of powdered activated carbon Carbopol WS, granulated carbon Z_4 of 1-3 mm granulation and bentonite Nobel. Selection of the appropriate kind of activated carbon was made based on the analysis of qualitative characteristics of home-made activated carbons. In order to enable the transfer of data characterizing the adsorption process in static conditions to practical conditions, tests were accomplished of adsorption process in dynamic conditions (5,6,7).

The tests of adsorption process were divided into two parts. The first one included laboratory tests made in order to determine the adsorption capacity of the tested activated carbon and Nobel bentonite in static conditions. Tests were made for the individual 7 solutions of dyes baths and also for 1 percent mixture of these baths. Physical and chemical constitution of tested solutions of dye baths and their mixture are given in Table 2.

Tests were also carried out for different concentrations of dyeing wastewater consisting of a mixture of 4 selected dyeing baths and assistants, the composition of which is given in Table 1.

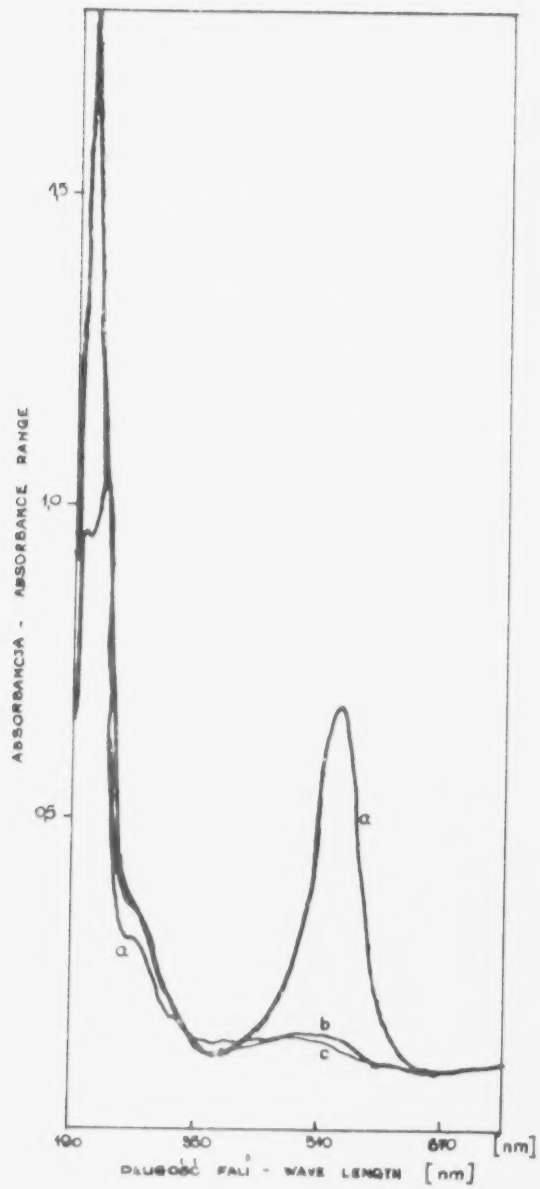
The second part included tests of adsorption process carried on continuously in adsorption columns with expanded bed of granulated carbon Z_4.

Laboratory investigations on continuous wastewater flow through adsorption column were carried out for 0.05 and 0.1 percent dyeing waster and assistants (Table 1). Laboratory tests of adsorption process were carried on with determination of the optimum time of reaction between wastewater and



Rys 35. Widma 0.5% ścieków farbiarskich.
a - przed i po bromowaniu
b - do zmiany barwy purpurowej na pomaranczową
c - żołto-pomarańczową
d - blado żołtą

Figure 35. Spectra of 0.5% dyeing wastewaters.
a - untreated and after bromination
b - until changing of purple hue to orange
c - yellow-orange
d - pale yellow



Rys 36. Widma ścieków farbiarskich
a - przed, i po bromowaniu
b - do zmiany barwy purpurowej na pomarańczową
c - i żółtą

Figure 36. Spectra of dyeing wastewaters
a - untreated and after treatment with bromine
b - until changing of purple hue to orange
c - to yellow

sorbent at the fixed temperature of 20 °C and the optimum dose of sorbent. The obtained values were the basis for determination of adsorption isotherm. Based on the obtained adsorption isotherm, the equilibrium adsorption capacity was defined for the given activated carbon and bentonite in reference to the tested solutions of dyeing baths and their mixtures. The adsorption capacity was then determined graphically as the ordinate for abscissa value = log Co presented in COD milligrams and dye milligrams for gram of activated carbon or bentonite.

Adsorption columns used in the investigations carried on in dynamic conditions were made from glass pipes with a diameter of 30 mm and 1500 mm high with a conical bottom ended with a supply conduit. The adsorption bed was hung on a metal net. Columns were filled with activated carbon Z_4 of 1-3 mm granulation. The height of adsorption bed was of about 900 mm, after scarification the height was about 1200 mm.

The technological system consisted of 2 columns in series. After exhausting the system, the first column was disconnected, the second column became the first one, and a column with new filling was set up as a second one. The adsorption columns were run as expanded beds, i.e., wastewater was applied from the bottom of the column.

Analytical checking of the adsorption process in dynamic conditions included determination of the following indices: pH, basicity, COD, color, anionic detergents.

Samples for the above mentioned determinations were taken during the whole period of adsorption columns studies at intervals of 15 to 30 minutes. Using the obtained results, relation curves were drawn of concentration of tested pollution indices in wastewater flowing out, and total volume of wastewater, which flow through the column in a given time period. From the obtained relations, a "puncture" time was defined for the bed of the second column, and a time of adsorption capacity exhausting for the first column. The adsorption capacity of a sorbent in dynamic conditions was calculated.

Tests in dynamic conditions were accomplished for the following load of adsorption bed:

Dyeing wastewater 0.1%

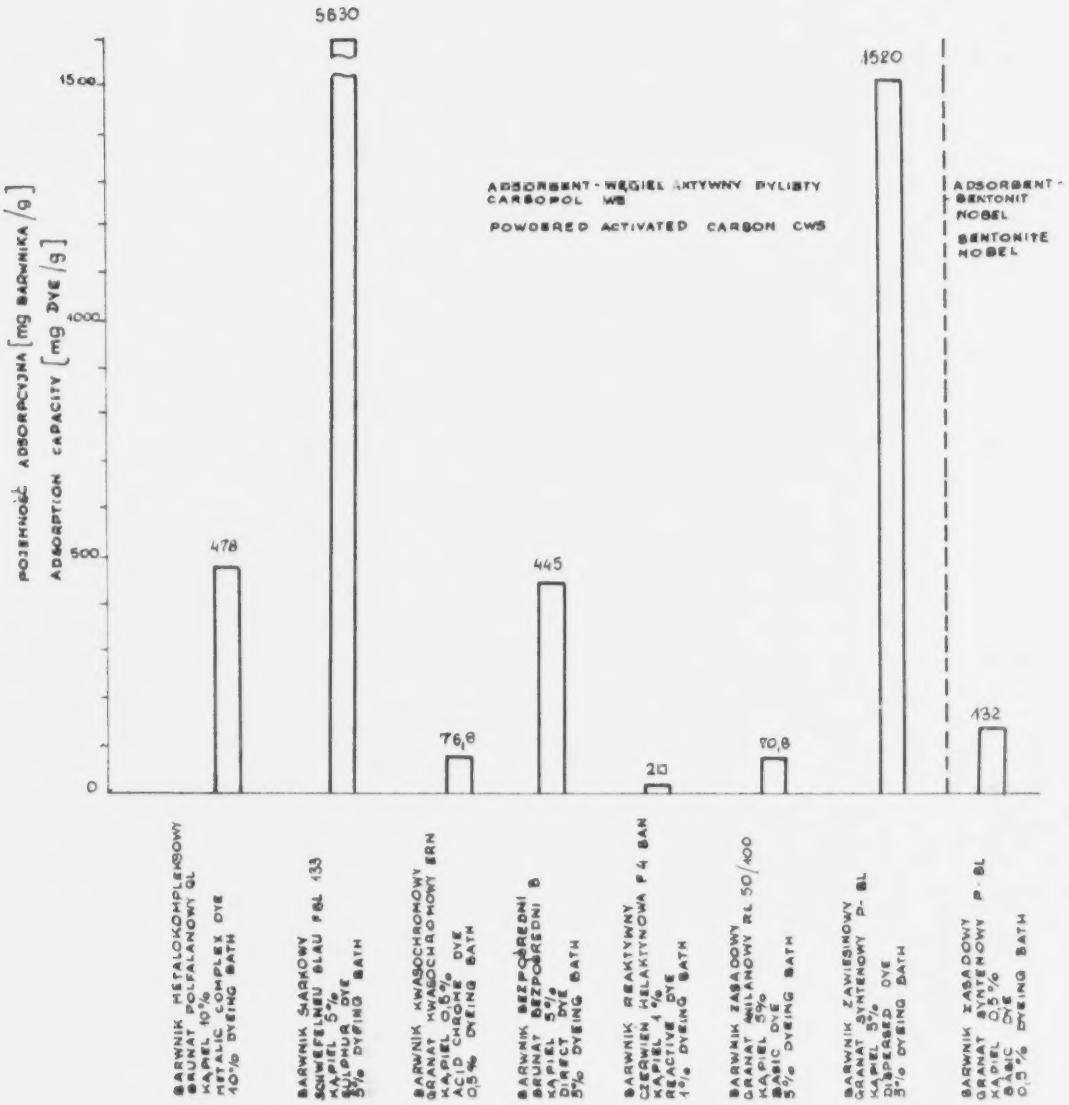
- 4.67; 6.23; 9.58; and 15.58 m^3/m^2

Dyeing wastewater 0.05%

- 20.0 m^3/m^2

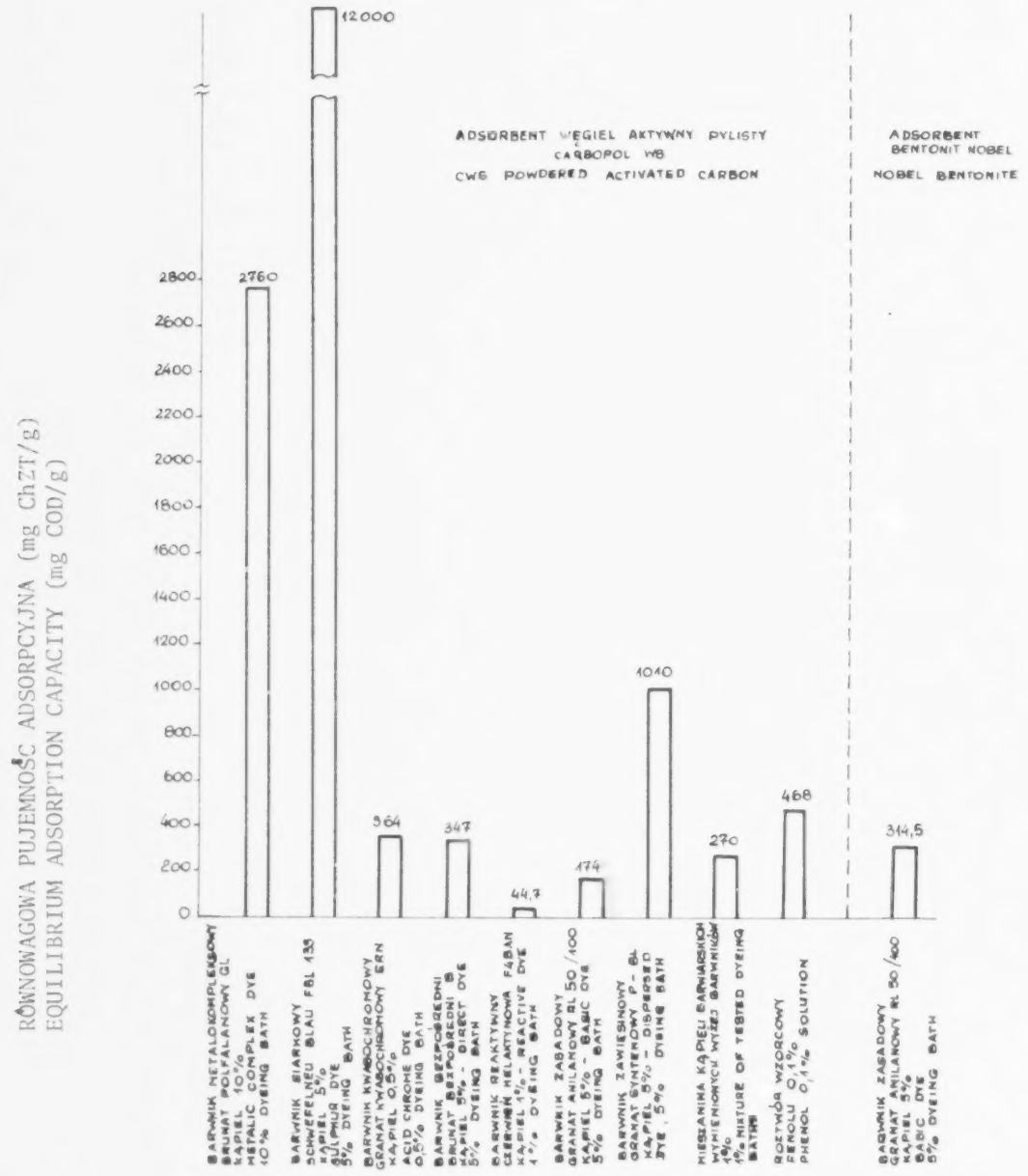
Discussion of the Investigations Results

The equilibrium adsorption capacities defined on the basis of test investigations for powdered activated carbon Carbopol WS, and bentonite Nobel expressed in mg of COD, and mg of dye for gram of sorbent have been presented in Fig. 37 and 38.


POJEMNOŚĆ ADSORPCYJNA [mg BARWNIKA/g]
ADSORPTION CAPACITY [mg DYE/g]
15 00
1000
500
0
5830
1520
478
445
76,8
20
70,8
132
ADSORBENT - WĘGIEL AKTYWNY PYLISTY CARBOPOL WS
POWDERED ACTIVATED CARBON CWS
ADSORBENT - BENTONIT NOBEL
BENTONITE NOBEL
BARWNIK METALOKOMPLEKSOWY BRUNAT POLFALANOWY GL KĄPIEL 10% METALIC COMPLEX DYE 10% DYEING BATH
BARWNIK SIARKOWY SCHWEFELNEU BLAU FBL 133 KĄPIEL 5% SULPHUR DYE 5% DYEING BATH
BARWNIK KWASOCHROMOWY GRANAT KWASOCHROMOWY BRN KĄPIEL 0,5% ACID CHROME DYE 0,5% DYEING BATH
BARWNIK BEZPOŚREDNI BRUNAT BEZPOŚREDNI B KĄPIEL 5% DIRECT DYE 5% DYEING BATH
BARWNIK REAKTYWNY CZERWIEŃ HELAKTYNOWA F4 BAN KĄPIEL 1% REACTIVE DYE 1% DYEING BATH
BARWNIK ZASADOWY GRANAT MILANOWY RL 50/400 KĄPIEL 5% BASIC DYE 5% DYEING BATH
BARWNIK ZAWIESINOWY GRANAT SYNTENOWY P-BL KĄPIEL 5% DISPERSED DYE 5% DYEING BATH
BARWNIK ZASADOWY GRANAT SYNTENOWY P-BL KĄPIEL 0,5% BASIC DYE 0,5% DYEING BATH

Rys 37. Porównanie wartości pojemności adsorpcyjnych badanego węgla aktywnego cws oraz bentonitu nobel, wyznaczonych w odniesieniu do roztworów wodnych kąpieli barwiarskich.

Figure 37. Equilibrium adsorption capacity of cws powdered activated carbon and nobel bentonite estimated for tested dyeing baths.



Rys 38. Porównanie wartości pojemności adsorpcyjnych badanego węgla aktywnego cws oraz bentonitu nobel wyznaczonych w odniesieniu do roztworów wodnych kąpieli barwiarskich i ich mieszaniny.

Figure 38. Equilibrium adsorption capacity of cws powdered activated carbon and nobel bentonite estimated for tested dyeing baths and their mixture.

Optimum effects of the adsorption process in static conditions obtained for selected solutions of dyeing baths and their mixtures of 1 percent concentration are presented in Table 8.

The obtained values of equilibrium capacity varied within a wide range, depending on the type of dye. The tested activated carbon showed the highest adsorptive capacity in case of sulfur, metallized, dispersed and direct dyes. Lower values were obtained for chrome and basic dyes.

The lowest value was obtained in case of reactive dyes. The adsorptive capacity of the activated carbon at 1 percent mixture of tested dyes was equal to 270 mg of COD/g.

When comparing the efficiency of color and COD removal obtained at optimum operational parameters of adsorption process, it was found that among two tested sorbents, only the activated carbon gave positive effects for all tested solutions of dye baths, while the bentonite had a significant adsorptive capacity only in case of the basic dye.

When considering the obtained adsorption rates for the individual dyes, the basic and sulfur dyes are very difficult to be adsorbed by activated carbon. It is apparent in the decreased efficiency of color and COD removal which after 30 minutes contact with adsorbent reach respectively 70.0 percent and 67.7 percent for basic dyes and 50.0 and 47.8 percent for sulfur dyes. Extending the adsorption time did not improve the efficiency of the process.

For the remaining dyes, the efficiencies of adsorption process were high, and after 60 minutes of contact time there was 90 to 99.8 percent color removal and 71 to 91 percent for COD (Table 8).

The decrease in efficiency of adsorption for dye baths in case of basic and sulfur dyes is likely due to molecule structure of these dyes and their ability to dissociate.

The tests were carried out for 0.1, 0.5 and 3.0 percent solutions of dyeing wastewater (Table 1), and the results obtained from these experiments are summarized in Fig. 39 and Table 9.

The adsorption process was carried out using powdered activated carbon Carbopol WS and for 0.1 percent dyeing wastewater. Additional tests were accomplished with granular activated carbon Z_4 which was later used in the investigations with continuous columns.

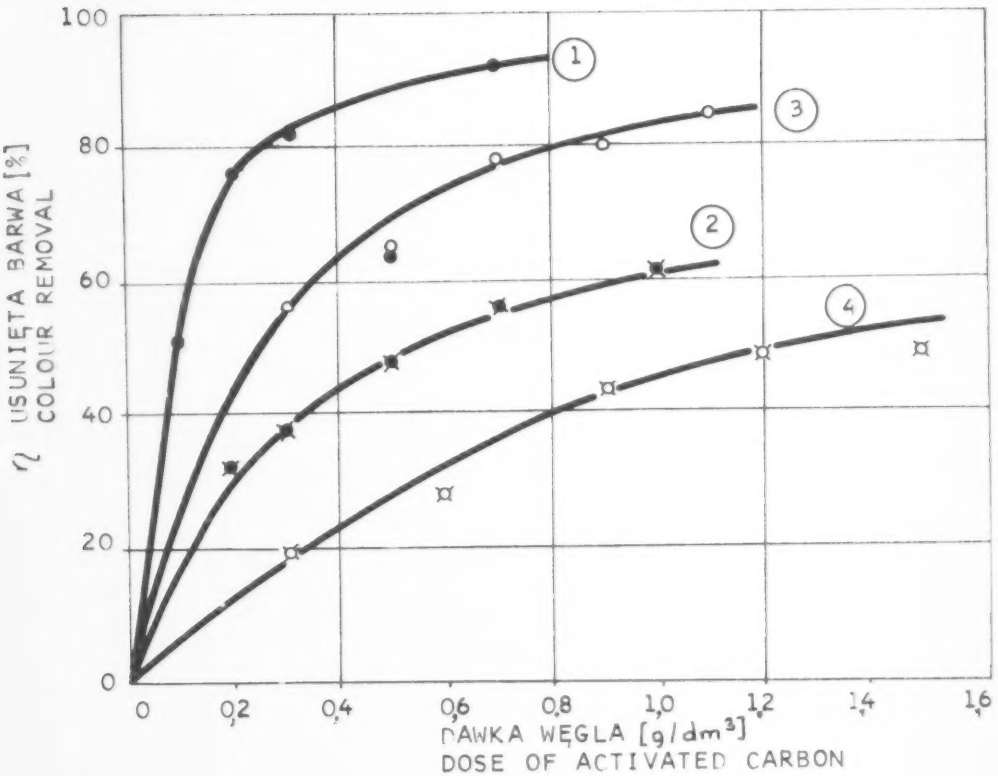
The adsorption in steady conditions was accomplished at natural pH and pH of 12, and adsorption process began immediately when pH about 12 was reached. The contact time of wastewater with NaOH solution applied for pH adjustment was 1-3 minutes.

From the obtained results, it can be stated that the adsorption process at original pH gives higher efficiency of color and COD removal in comparison with the efficiency of adsorption process at pH of about 12.

TABLE 8. ADSORPTION OF DYEING BATHS BY POWDERED ACTIVATED CARBON AND BENTONITE

Dyes	Dye concentration %	Dye concentration mg/dm^3	Initial COD mg/dm^3	Adsorbent	Adsorbent dosage g/dm^3	Optimal adsorption time min	pH	Color removal %	COD removal %	Anion detergents removal %
Metallic-complex dye Polfalen brown GL	10	2500	7120	activated carbon	20	30	3.4	97.0	76.0	98.0
Sulfur dye - Schwefelneu blau FPL	5	2000	4150	-"-	20	30	10.5	50.0	47.8	94.4
Acid-chrome dye - Acid-chrome blue GRN	5	150	676	-"-	20	60	8.6	99.8	90.6	88.0
Direct dye - Direct brown B	5	1000	1140	-"-	20	60	9.7	96.0	89.6	x
Reactive dye - Helactyn red F BAN	1	3000	394	-"-	20	60	9.1	96.0	64.9	x
Basic dye - Aniline blue RL 50/100	5	1250	2675	-"-	20	30	5.1	90.0	71.1	xx
Basic dye - Aniline blue RL 50/100	3	1250	2675	bentonite	20	30	2.6	100.0	81.1	xx
Dispersed dye - Synten blue P-BL	5	3000	4200	activated carbon	20	30	9.3	70.0	67.7	xx
Mixture of above dyeing baths	1	330	790	-"-	20	60	9.2	-	75.3	xx

x nonionic detergents
xx the dye reacts with chloroform, giving colored compound



Rys 39. Porównanie efektów usuniecia barwy w procesie adsorpcji na pylistym węglu aktywnym cws dla różnych wartosci pH.

Figure 39. Color removal by powdered activated carbon adsorption effect of pH adjustment to 12.

TABLE 9. ADSORPTION OF DYEING WASTEWATER BY ACTIVATED CARBON CARBOPOL WS - BASED ON JAR TESTS

Concentration of dyeing wastewaters	Dosage of activated carbon	Time adsorption	pH	Color[x] removal	COD removal
%	g/dm^3	min	-	%	%
0.1	0.3	45	7.20	82	40
0.1	0.3	45	~12	38[xxx]	43[xxx]
	1.0	45	~12	61[xxx]	54[xxx]
0.1	1.0[xx]	60	7.64	67	13
	3.0	60	8.72	85	37
0.5	0.5	45	7.62	68	39
	1.0	45	7.80	83	40
0.5	0.5	45	~12	30[xxx]	18[xxx]
	1.0	45	~12	44[xxx]	30[xxx]
	2.0	45	~12	60[xxx]	33[xxx]
3.0	6.0	30	8.0	83.5	40

[x] Comparison method
[xx] Granular activated carbon Z_4
[xxx] The results have been estimated based on initial values of COD and color of wastewaters after pH adjustment to 12

Total efficiency of color reduction at pH 12 for tested wastewater concentrations of 0.1 and 0.5 reached about 50 percent of effects obtained in the adsorption process at original pH (Fig. 39).

The plotted isotherms of pollution adsorption expressed in terms of the COD indicate, that a large amount of substances, which are not adsorbed by tested activated carbon, is present in the effluent.

The obtained straight plots intersect the adscissa (log concentrations of adsorbed substances), not indicating any point on the ordinate. Fig. 40 is an example of adsorption isotherms for dyeing wastewater of 0.5 percent concentration.

When considering the color as a parameter of dyeing wastewater pollution, the shape of adsorption isotherms obtained provided an evaluation of the equilibrium capacity of tested carbon. Depending on dyeing wastewater concentration, the equilibrium capacities in terms of carbon Carbopol WS were as follows: from 958 percent of color for 0.1 percent wastewater, 331 percent of color for 0.5 percent wastewater to 32 percent of color for 3.0 percent dyeing wastewater.

For the laboratory tests on the continuous adsorption columns, dyeing wastewater of 0.05 percent and 0.1 percent concentration were chosen. The process was carried out at the original pH at room temperature using granular activated carbon Z_4 for which the determined equilibrium capacity expressed in terms of COD was equal to 5 mg COD/g.

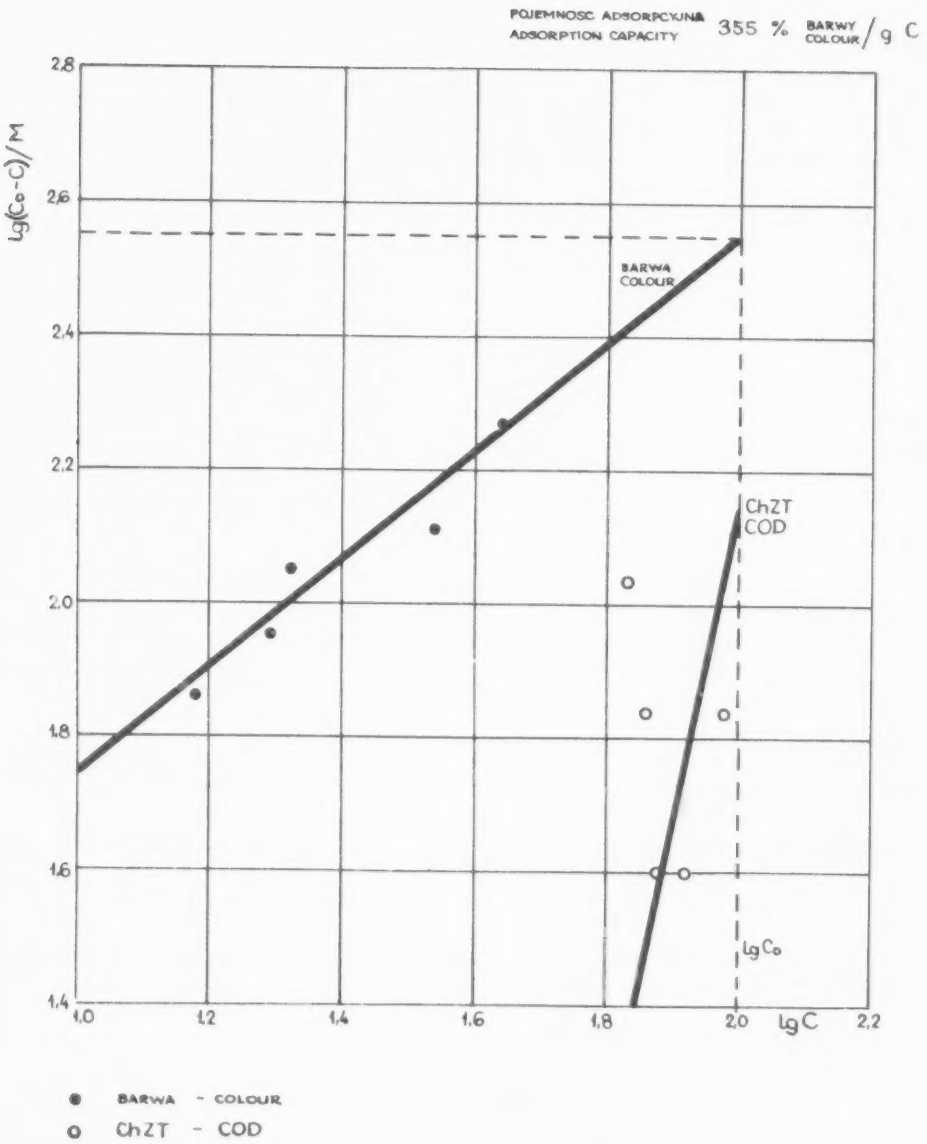
The obtained results of color removal gave the basis for selection of surface loading for further laboratory investigations.

For the laboratory investigations carried on for two columns linked in series, the surface loadings selected were: 9.58 m^3/m^2 for 0.1 percent wastewater and 20.0 m^3/m^2 for 0.05 percent wastewater.

The conditions and the results for the two columns linked in series were as follows:

0.1% dyeing wastewater:

- average flow rate of wastewater through columns - 6.9 dm^3/h
- average surface loading - 9.58 $m^3/m^2.h$
- time of contact of wastewater with adsorbent in entire system - 10 min (calculated for non-filled working space of column)
- COD of wastewater before adsorption - 45 mg O_2/dm^3
- residual COD in effluent after adsorption - average 15 mg/dm^3, range from 10 to 20 mg O_2/dm^3. Critical concentration of breakthrough was 20 mg O_2/dm^3 COD.
- efficiency of color removal in total system - 80%
- efficiency of COD removal in total system - 55-78%, 66% in average
- an average adsorption capacity of total system - 3.0 mg COD/g
- services time of system before the break point - 4.5 hours



Rys 40. Izoterma procesu adsorpcji na pylistym węglu aktywnym carbopol ws. Ścieki farbiarskie - 0.5% proces prowadzony dla pH naturalnego.

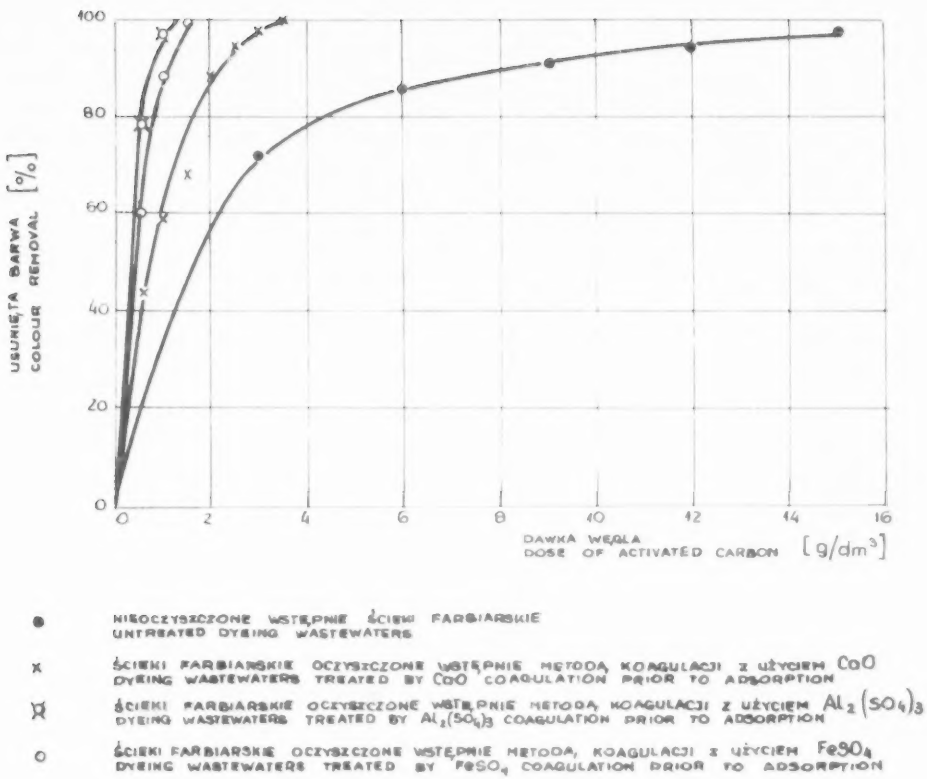
Figure 40. Adsorption isotherm on powdered activated carbon - carbopol ws for 0.5% dyeing wastewaters without pH adjustment.

0.05% dyeing wastewater:

- average flow rate of wastewater through column - 14.4 dm^3/h
- average surface loading - 20 $m^3/m^2.h$
- time of contact of wastewater with adsorbent in entire system - 5 minutes (calculated for non-filled working space of column)
- COD of wastewater before adsorption - 25 mg O_2/dm^3
- COD of wastewater remaining after adsorption - average 5 mg O_2/dm^3, range to 16 mg/dm^3. Critical concentration for which breakpoint was defined - 16 mg/dm^3
- efficiency of color removal in total system - 98-100%
- efficiency of COD removal in total system - 80%
- an average adsorption capacity of total system - 4 mg COD/g
- service time of system before breakpoint - 4 hours

If the color removal values were applied to evaluate efficiency of the adsorption process in continuous columns instead of COD values, the service time would be extended twice.

Substantial decrease of the indispensable dose of adsorbent can be obtained by earlier introduction of the coagulation process. The comparison of the obtained efficiencies of color removal in the adsorption process without wastewater coagulation and after coagulation with 6000 mg CaO/dm^3, 250 mg $Al_2(SO_4)_3/dm^3$ and 500 mg $FeSO_4/dm^3$ was presented in Fig. 41.



Rys 41. Porównanie efektów usunięcia barwy w procesie adsorpcji 3% ściekow farbiarskich na pylistym węglu aktywnym

Figure 41. Color removal by powdered activated carbon adsorption 3% dyeing wastewaters effect of varying activated carbon doses

SECTION 6

BIOLOGICAL METHODS FOR DYEINC WASTEWATER TREATMENT

6.1 THE ACTIVATED SLUDGE METHOD

Methodology and the Scope of Studies

The studies on dyeing wastewater treatment were carried out in three stages. In the first stage some testing runs were done using the lab-scale units, periodically loaded with municipal wastewater with addition of some selected substances typical for dyeing wastewater. In the first series, laboratory investigations used continuous feeding with municipal wastewater blended with six selected substances specific for dyeing wastewater. In these investigations, an aeration tank of 5.7 dm^3 capacity was used.

The second series of investigations with continuous wastewater feeding was carried out with municipal wastewater containing 0.1 volume percent of a mixture of selected dye baths and assistants (Table 1).

The studies dealt with a wide range of concentrations of the applied substances to get as much as possible explicit information about their effect on the biochemical processes.

The batch tests were performed using seven laboratory scale aeration tanks with activated sludge, periodically fed with wastewater.

Six wastewater mixtures and a reference sample were applied to the tests.

The wastewater mixtures were composed from raw municipal wastewater and the following additives: reactive dye - Lunasol Rot 5B, basic dye - Aniline BLN, sulfuric dye - Sulfuric Brown, welan dye - Welan Brown, assistant - fixing agent WOM, assistant-dispersing agent NNO. Each of them was at a concentration of 300 mg/dm^3.

The initial activated sludge was obtained from the municipal wastewater treatment plant. Before the studies began the sludge was first acclimated for four days to a mixture of municipal wastewater containing 0.1 volume percent of dyeing wastewater. To achieve an increased load of activated sludge, the test investigations were carried out with raw municipal wastewater.

The laboratory models used for these studies were of 3 dm^3 capacity, and the initial volume of the mixed liquor (culture) was of 1.5 dm^3. The initial content of activated sludge suspended solids was about 1.0 g/dm^3. Activated

sludge loadings in terms of BOD_5 and COD in g/g MLVSS·d for particular activated sludge cultures were as follows:

	BOD_5	COD Not filtered	COD Filtered
1. Municipal wastewater	0.084 - 0.160	0.150 - 0.358	0.061 - 0.290
2. Municipal wastewater with addition of reactive dye	0.102 - 0.185	0.300 - 0.705	0.282 - 0.583
3. Municipal wastewater with addition of basic dye	0.052 - 0.156	0.360 - 0.890	0.290 - 0.530
4. Municipal wastewater with addition of sulfuric dye	0.047 - 0.155	0.240 - 0.462	0.116 - 0.356
5. Municipal wastewater with addition of welan dye	0.061 - 0.158	0.429 - 0.954	0.384 - 0.754
6. Municipal wastewater with addition of fixing agent WOM	0.0236 - 0.067	0.270 - 0.454	0.171 - 0.315
7. Municipal wastewater with addition of dispersing agent NNO	0.074 - 0.148	0.220 - 0.732	0.220 - 0.547

Discussion of the Results

The pollution concentration of municipal wastewater varied during the course of investigations. The average values of BOD_5 and COD of the proportioned wastewater were respectively about 90 mg/dm^3 and 117 mg/dm^3. Simultaneously, significant fluctuations in BOD_5 values reaching a mean value of 40 mg/dm^3 were noted. Much lower fluctuations were observed in the case of COD of treated wastewater. The major part of the results varied in the range from 40 to 43 mg/dm^3. The pollution removal from wastewater during the control tank processing was about 56 percent and 65 percent, respectively for BOD_5 and COD.

A decrease in the mixed liquor suspended solids content in the aeration tanks was observed during the studies. The decrease was from the initial value of about 800 mg/dm^3 (volatile parts) to about 480 mg/dm^3. The only exception was for the tank fed municipal wastewater with addition of fixing agent WOM. Simultaneously a decrease of activated sludge volume index from about 170 cm^3/g to 128 cm^3/g was observed.

An explicit determination of the inhibiting influence of dyes or assistants on the activated sludge process appears to be difficult based on the obtained results, however it was apparent that the dye addition to municipal wastewater disturbed the process.

The analysis of BOD_5 and COD removal effect from the municipal wastewater mixed with dyes and/or assistants gave very interesting results. It revealed that the addition of reactive dye and dispersing agent NNO caused an increase in BOD_5 of about 50 mg/dm^3. Simultaneously a twice or three times increase in COD of filtered samples was observed for each case. A significant BOD_5 reduction in a range from 50 percent to 80 percent was noted for all tested series. The gained COD removal effects ranged from 10 to 35 percent. Comparing the absolute amounts of removed pollution loads expressed in BOD_5 and COD, it can be stated that both biochemical, as well as the chemical oxygen demand, have been similarly reduced.

Discussion on the Results of Laboratory Studies Using A Continuous Wastewater Feeding System

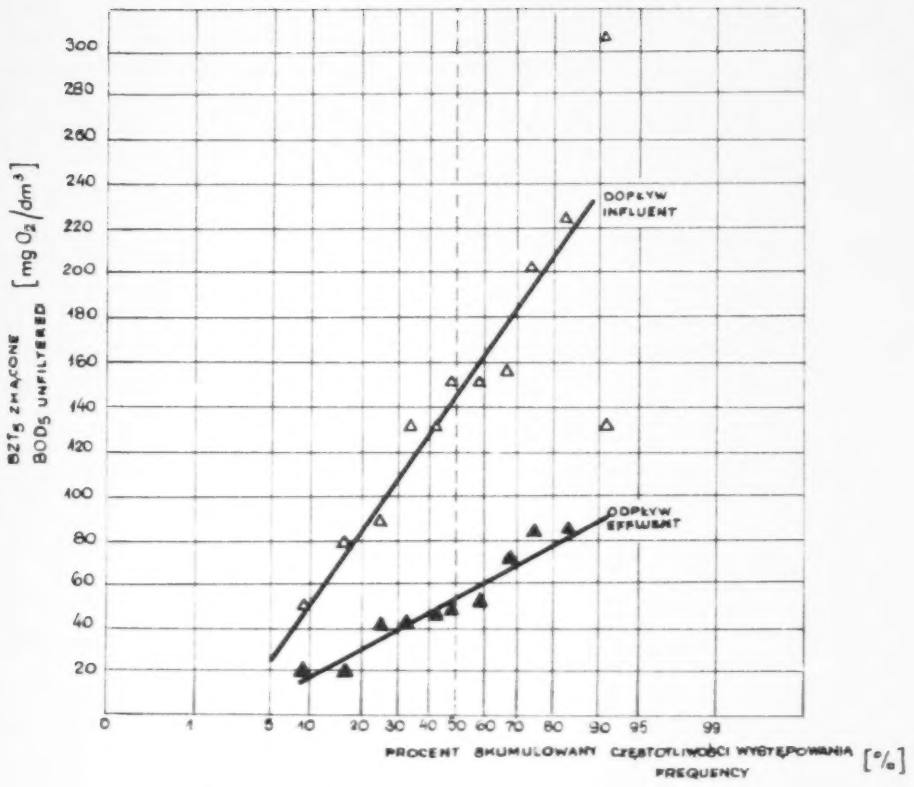
The tested wastewater mixture used for the series of tests with continuous feeding was characterized by relatively high BOD_5 and COD values. The average BOD_5 values in the first series were about 145 mg/dm^3; whereas in the second series, the BOD_5 values increased to about 210 mg/dm^3. Simultaneously, there was not such a significant difference in COD values in the both described test series. The average COD values for the filtrated samples in the first series were of about 253 mg/dm^3 and for the second series 235 mg/dm^3.

The Figures 42 - 45 show that the variability of COD and BOD_5 values was rather significant.

In the subsequent series of technological investigations, the following operational parameters were used:

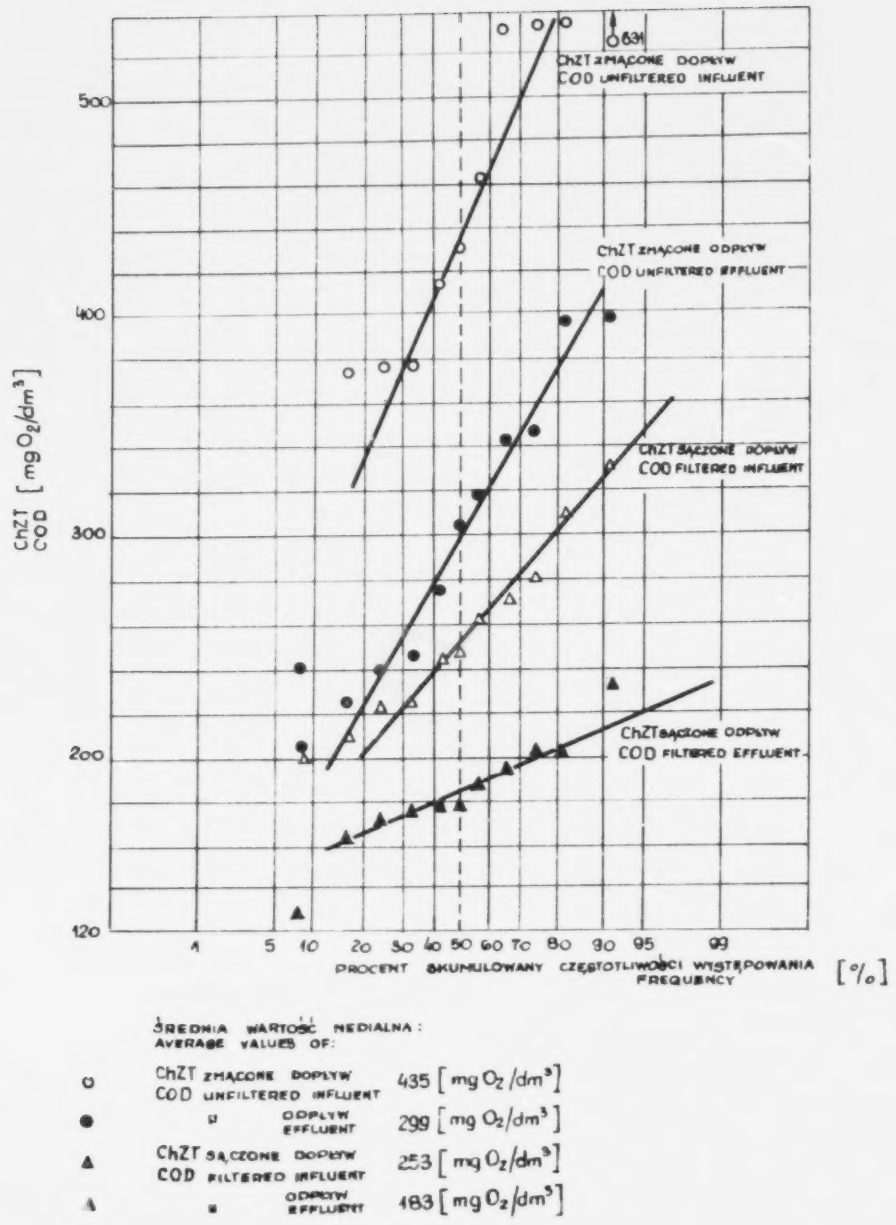
The average pollution concentrations in crude and treated wastewater as well as the treatment effects are listed below:

Parameter	1st Series			2nd Series		
	Inflow	Outflow	Treatment Effect	Inflow	Outflow	Treatment Effect
	mg/dm	mg/dm^3	%	mg/dm^3	mg/dm^3	%
BOD_5 not filtered	145	52	64	210	40	81
COD not filtered	435	299	31	415	150	64
COD filtered	253	183	28	235	80	66
Total suspended solids	175	140	20	163	70	57
Suspended solids - volatile parts	128	98	24	110	50	55



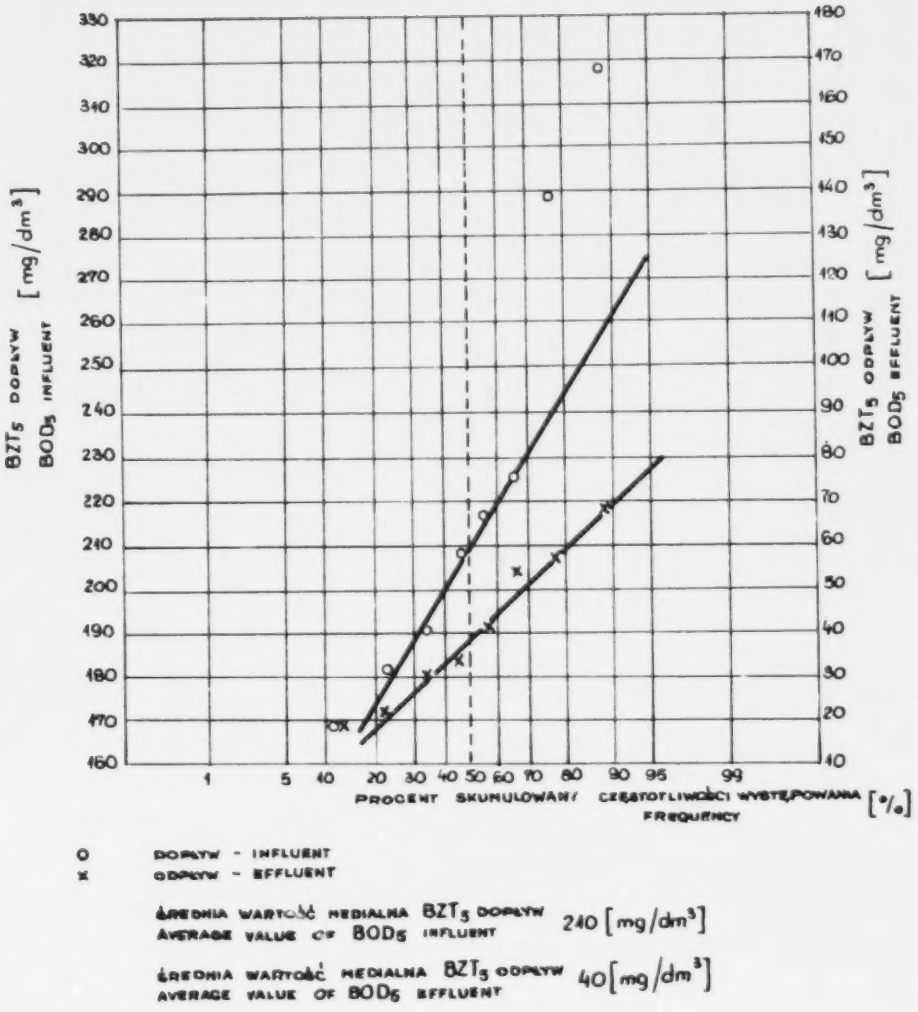
Rys 42. Częstotliwość występowania wartości bzt_5 w ściekach dopływających I odpływających z komory napowietrzania. Seria I.

Figure 42. Frequency of BOD_5 unfiltered. Series I.



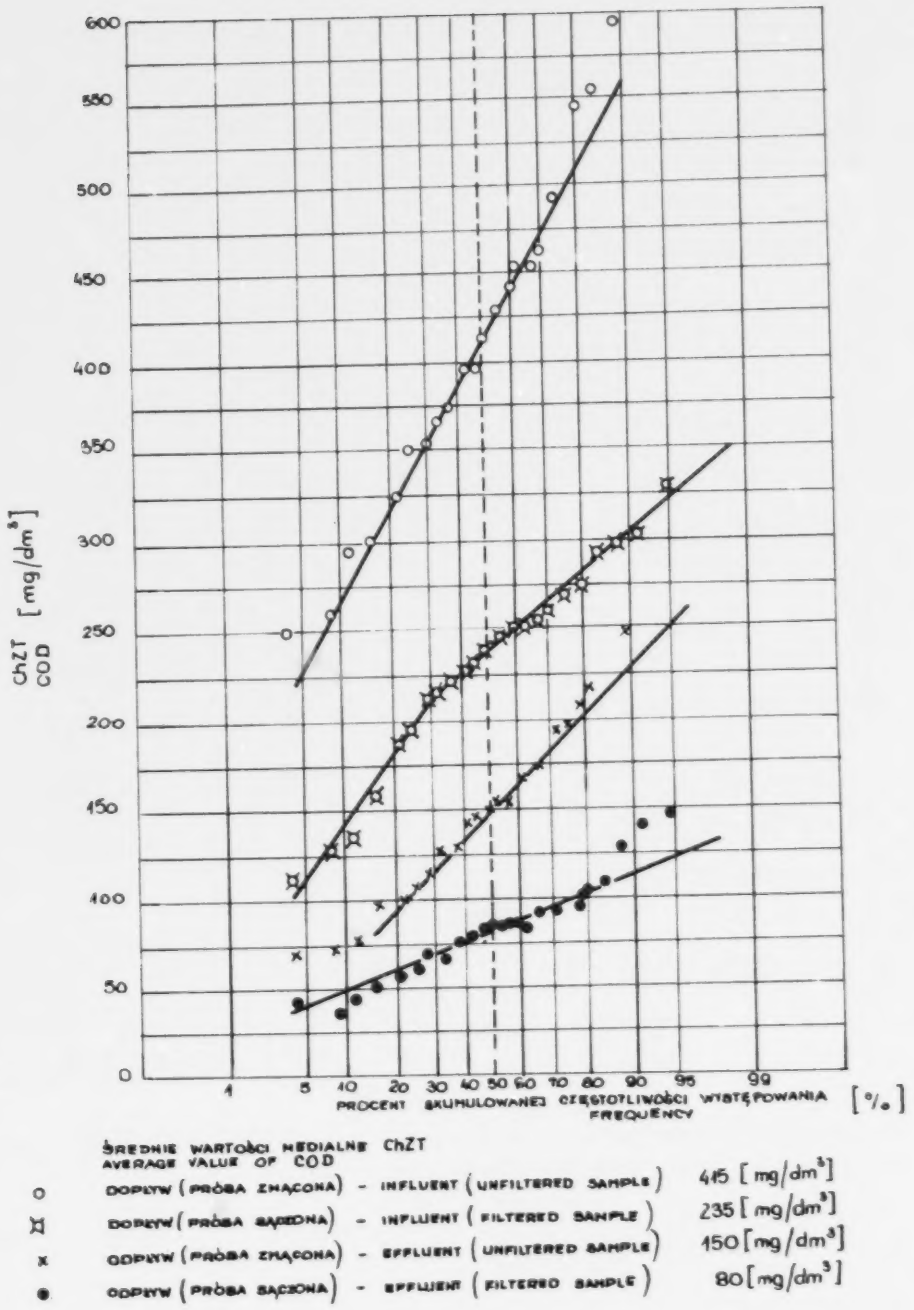
Rys 43. Częstotliwość wystepowania wartości chzt w ściekach dopływających i odpływających z komory napowietrzania. Seria I.

Figure 43. Frequency of influent COD and effluent COD. Series I.


BZT5 DOPŁYW BOD5 INFLUENT [mg/dm3]
BZT5 ODPŁYW BOD5 EFFLUENT [mg/dm3]
PROCENT SKUMULOWANEJ CZĘSTOTLIWOŚCI WYSTĘPOWANIA FREQUENCY [%]
o DOPŁYW - INFLUENT
x ODPŁYW - EFFLUENT
ŚREDNIA WARTOŚĆ MEDIALNA BZT5 DOPŁYW AVERAGE VALUE OF BOD5 INFLUENT 240 [mg/dm3]
ŚREDNIA WARTOŚĆ MEDIALNA BZT5 ODPŁYW AVERAGE VALUE OF BOD5 EFFLUENT 40 [mg/dm3]

Rys 44. Częstotliwość występowania wartości BZT_5 w ściekach dopływających i odpływających z komory napowietrzania. Seria II.

Figure 44. Frequency of influent, effluent BOD_5. Series II.



Rys 45. Częstotliwość występowania ChZT w ściekach dopływających i odpływających z komory napowietrzania. Seria II.

Figure 45. Frequency of influent, effluent COD. Series II.

The operating parameters for activated sludge process used to obtain the above data were as follows:

		1st Series	2nd Series
Time of wastewater aeration with activated sludge	h	6.5	7.0 and 11.5
Sedimentation time in a secondary settling tank	h	2.2	2.8 and 4.5
The loading of activated sludge volatile parts by BOD_5 load	g/g·d	0.23 - 1.04	0.14 - 0.52
The loading of activated sludge volatile parts by COD not filtered	g/g·d	0.70 - 3.35	0.18 - 0.91
The loading of activated sludge volatile parts by COD filtered	g/g·d	0.42 - 2.82	0.08 - 0.61

The contents of activated sludge in an aeration tank:

		1st Series	2nd Series
Total suspended solids	g/dm^3	1.82 - 0.30	1.65 - 2.80
Suspended solids - volatile parts	g/dm^3	1.43 - 0.22	1.10 - 2.23
Average concentration of suspended solids - volatile parts	g/dm^3	1.01	1.83

Despite the differences in wastewater concentrations in both series, the test results are listed and discussed together.

For simplification, because of the uncontrolled fluctuation in concentration of the fed substrate and volatile parts of suspended solids of activated sludge in aeration tanks, the above mentioned series have been divided into several intervals. In the 1st series two intervals and in the 2nd series eight intervals have been distinguished.

The average BOD_5 and COD values for a filtered sample, the activated sludge suspended solids, and the wastewater retention time in aeration tank for the particular distinguished intervals were determined. The determined average values were applied to the calculation of the dyeing wastewater

treatment efficiency index. The average values for the first series of continuous testing are presented in Table 10. For the second series of testing, the average values are listed in two tables, i.e., 11 and 12.

A comparability of the first and second series results has been compared by analyzing the BOD_5 and COD reduction efficiency versus the pollution loading (Fig. 46).

A reduction of BOD_5 in the range from 60 percent to 90 percent was reached by the pollution loading of values from 0.2 to 0.95 g/g·d.

Presenting the obtained results as a dependence of the activated sludge efficiency ($W = k \cdot S$) from the loading (L), there exists a possibility (Fig. 47) to comprise all results by applying the following general mathematical expression:

$$W = 2 \frac{L}{2.2 + L}$$

where W = efficiency in D^{-1}
L = sludge loading in g/g·d

Using the same method, the comparable COD (filtered sample) results for the first and second continuous testing series have been obtained. However, it must be noticed a low reduction efficiency of COD (Fig. 46) for loadings extending over 1.0 g/g·d. This efficiency was in the range from 20 percent to 30 percent. It also appeared that the chlorination process of the biologically treated wastewater did not lead to a significant increase of the COD removal effects. However, in two cases a 40 percent and 47 percent removal of unfiltered sample COD by the presence of 50 and 60 mg/dm^3 doses of chlorine was observed, while the COD removal for filtered sample was only about 12 percent.

The above presented facts may relate to the difficult biochemical regeneration and incomplete chemical aeration of the added dyes and assistants.

The wastewater treatment through the activated sludge process has not resulted in the color removal. In general, the color was unchanged except for the sporadical instances in both series when about 20 percent of color removal was attained. The other investigations reveal that the color reduction can be effectively obtained in the chlorination process of biologically treated wastewater.

Applying a chlorine dose of 34 mg/dm^3 concentration, a complete decolorization can be obtained (Fig. 48). The complete decolorization can be obtained by using the adsorption process on activated carbon, as well. A complete removal of the fine suspended matter on a sand filter is required before applying the above mentioned adsorption method. The sand filtration leads also to a COD and BOD_5 removal.

TABLE 10. PARAMETERS OF BOD_5 AND COD REMOVAL PROCESS IN DYEING WASTEWATER TREATMENT BY ACTIVATED SLUDGE METHOD - I SERIES

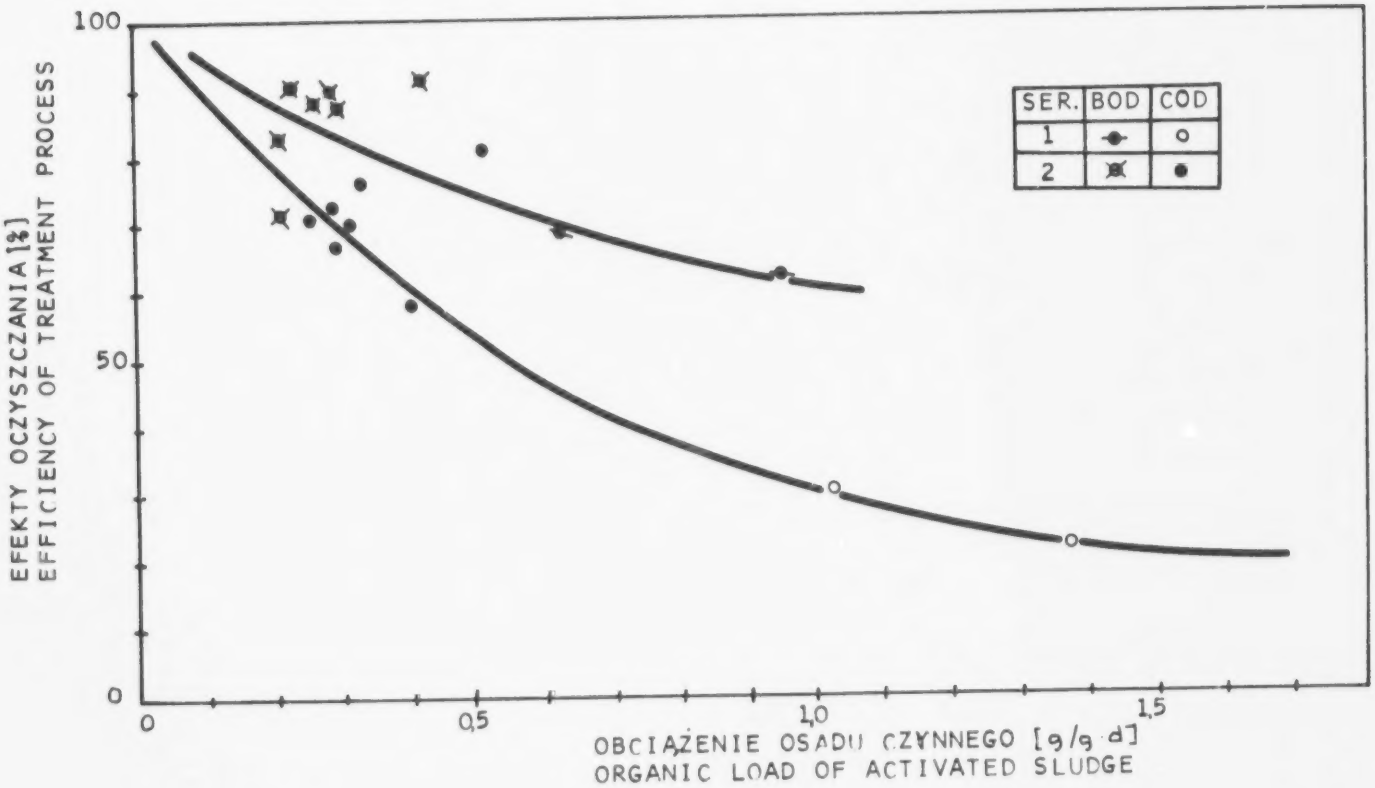
Parameters		Investigation period 1	2	Parameters		Investigation period 1	2
S_a= influent BOD_5 mg/dm^3		152	154	S_a= infl. COD filtered mg/dm^3		223	263
S = effluent BOD_5 mg/dm^3		57	47	S = effl. COD filtered mg/dm^3		176	183
t_z= aeration time	h	6.08	5.47	t_z= aeration time	h	6.08	5.37
X_a= MLVSS mg/dm^3		640	1140	X_a= MLVSS mg/dm^3		640	1140
η = % removal		62.5	69.5	η = % removal		21.2	30.4
$L = \frac{S_a}{X_a . t}$	g/g.d	0.938	0.604	$L = \frac{S_a}{X_a . t}$	g/g.d	1.375	1.031
1/L	d	1.067	1.656	1/L	d	0.727	0.970
$S_a - S$	g/g.h	0.0244	0.0175				
$\overline{X_a . t}$	g/g.h	0.586	0.419				
$\frac{X_a \cdot t}{S_a - S}$	g/g.d	1.707	2.384				

TABLE 11. PARAMETERS OF BOD_5 REMOVAL PROCESS IN DYEING WASTEWATER TREATMENT BY ACTIVATED SLUDGE METHOD - SERIES II

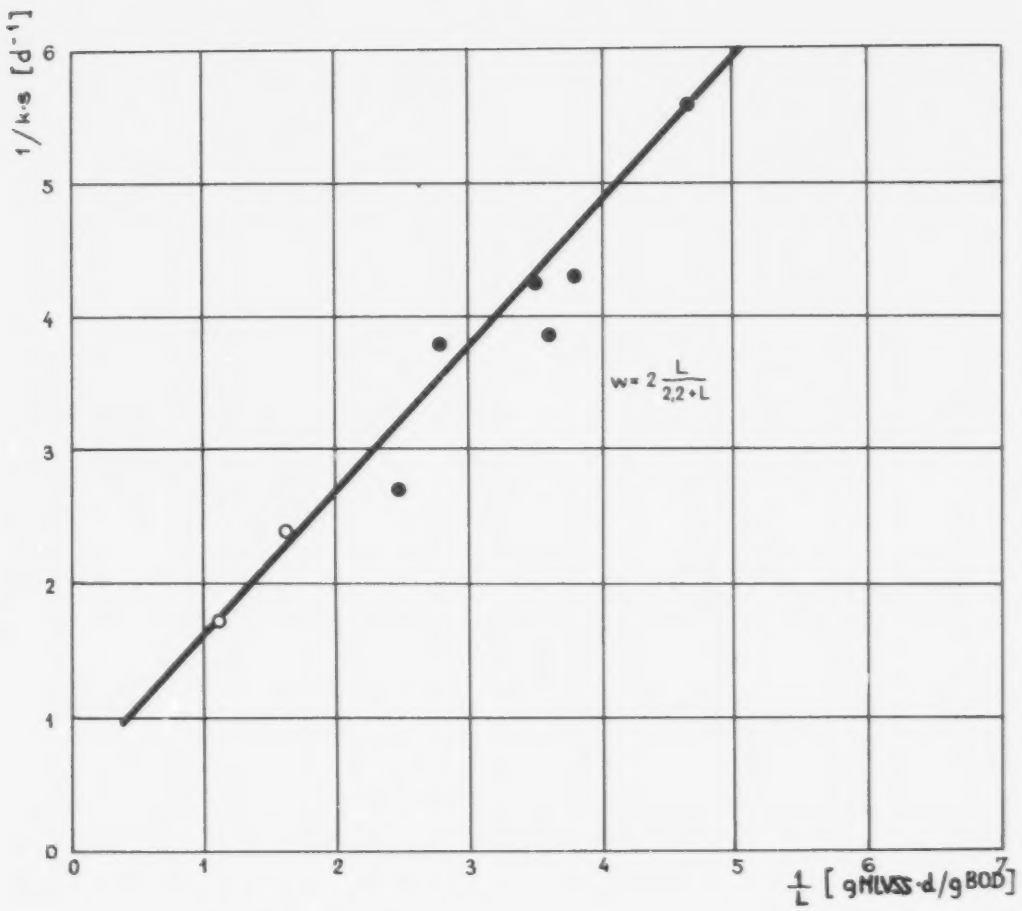
Parameters		Investigation Period 1	2	3	4	5	6	7	8
S_a = influent BOD_5	mg/dm^3	216	190	218	288	169	224	182	208
S = effluent BOD_5	mg/dm^3	69	54	41	32	30	21	18	57
t_z = aeration time	h	11.5	11.5	11.3	11.6	11.3	8.0	7.7	6.8
X_a = MLVSS	mg/dm^3	1800	1900	1600	2250	1650	1650	2010	2050
η = % removal		68.1	71.6	81.2	88.9	82.2	90.6	90.1	72.6
$L = \frac{S_a}{X_a.t}$	g/g.d	0.250	0.209	0.289	0.265	0.218	0.407	0.282	0.358
1/L	d	4.000	4.785	3.460	3.776	4.587	2.457	3.546	2.793
$\frac{S_a - S}{X_a.t}$	g/g.h	0.0071	0.0062	0.0098	0.0098	0.0075	0.0151	0.0106	0.0118
	g/g.d	0.170	0.149	0.235	0.235	0.179	0.367	0.254	0.260
$\frac{X_a.t}{S_a - S}$	d	4.09	5.71	4.26	4.26	4.26	5.59	3.93	3.85

TABLE 12. PARAMETERS OF COD REMOVAL PROCESS IN DYEING WASTEWATER TREATMENT BY ACTIVATED SLUDGE METHOD - SERIES II

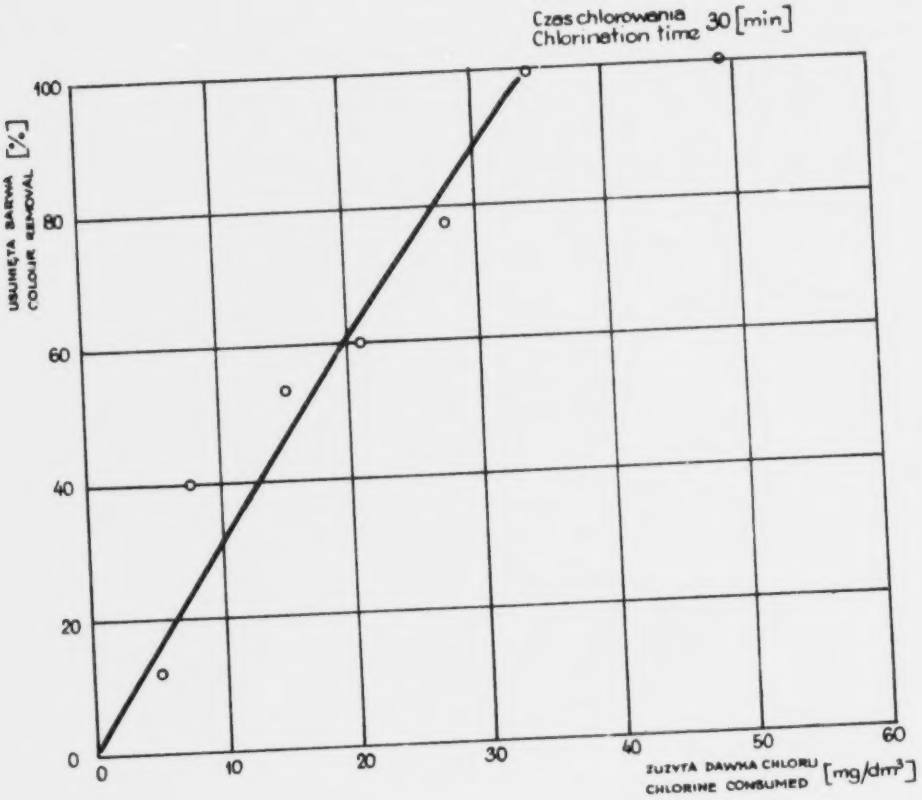
Parameters	Investigation Period 1	2	3	4	5	6	7	8
S_a = influent COD mg/dm^3	241	236	242	300	233	230	220	303
S^a = effluent COD mg/dm^3	142	64	72	88	75	97	51	57
t_z = aeration time h	11.5	11.5	11.3	11.6	11.3	8.0	7.7	6.8
X_a = MLVSS, mg/dm^3	1800	1900	1600	2250	1650	1650	2010	2050
η = % removal	41.1	72.9	70.2	70.7	67.4	57.8	76.8	81.2
$L = \frac{S_a}{X_a.t}$ g/g.d	0.280	0.259	0.321	0.276	0.299	0.418	0.341	0.52



Rys 46. Zależność efektów usunięcia BZT i ChZT od obciążenia.
Figure 46. Correlation between organic load of activated sludge and BOD_5 and COD removal.



Rys 47. Wydatek osadu czynnego.
Figure 47. Efficiency of activated sludge process.



Rys 48. Efekt usunięcia barwy w zależności od zużytej dawki chloru w procesie chlorowania ścieków farbiarskich 0.1%, uprzednio oczyszczonych metodą osadu czynnego.

Figure 48. Relationship between color removal and chlorine consumed in chlorination process of 0.1% dyeing wastewaters treated by activated sludge method.

No correlation was found between the measured oxygen uptake rates by activated sludge and the COD and BOD_5 removal effects.

A relatively constant oxygen uptake in a range of 0.21 to 0.29 g O_2/g·d was observed for loadings ranging from 0.2 to 0.95 g/g·d.

The phosphates content in the treated wastewater became stabilized at a markedly high level, i.e., 18 mg/dm^3. After the treatment, a significant phosphates content decrease of about 50 percent was noted. This likely can be explained by the phosphates conversion into complex compounds.

An explicit reduction of the anion detergents as a result of wastewater treatment has also been observed. If the initial detergents concentration was of about 12 mg/dm^3, after treatment the concentration decreased to 1.7 mg/dm^3 which is an 86 percent detergent removal.

In analyzing the nitrogen compounds changes, it was noted that in the first testing series, the ammonia nitrogen average content oscillated between 15 mg/dm^3 to 20 mg/dm^3. These were rather low concentrations, however because of the BOD_5:N ratio, it is of some importance. The lack of substantial differences in ammonia nitrogen concentrations, due to the wastewater treatment, was a distinctive conclusion from these investigations (Fig. 49).

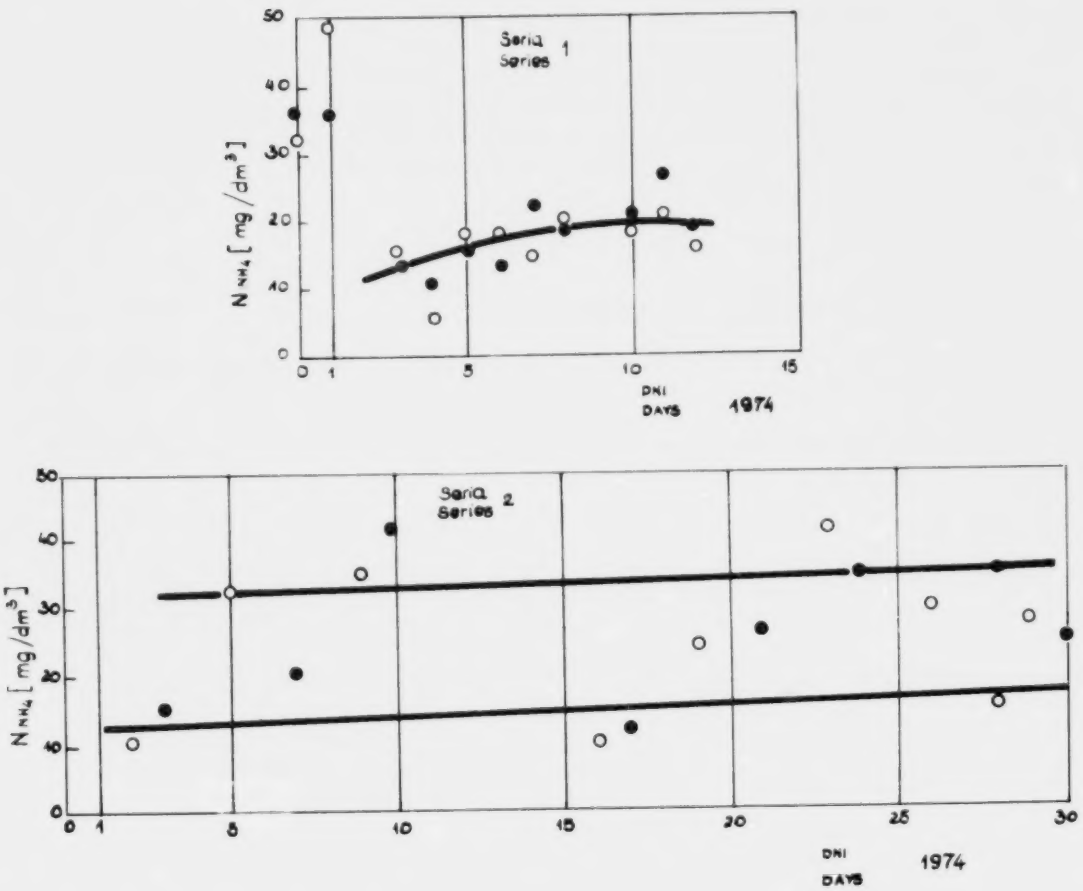
Similarly, in the second testing series, the ammonia nitrogen concentrations did not vary significantly. If in the supplied crude wastewater the ammonia nitrogen concentration varied in the range of 15 to 35 mg/dm^3, the similar increased concentration level was observed in the treated wastewater (Fig. 49).

The inhibition of the nitrification process was additionally proved by the analysis of nitrite and nitrate nitrogen concentration changes. No significant changes in the above mentioned compounds concentrations were determined as a result of the applied treatment method. Although the tested pollution loadings, namely 0.20 to 0.95 mg/g.d, were sufficiently high to inhibit the intensive growth of nitrification microorganisms, at the lower loadings at least the initiation of nitrification process might be expected.

The phenols concentration in the tested wastewater was equal to 0.7 mg/dm^3. The process of wastewater treatment was found to be effective for phenol removal, as was expected. The phenol concentration in the effluent discharged from the secondary settling tank was of about 0.016 mg/dm^3, thus 98 percent of phenol was removed.

The tested wastewater contained heavy metals derived from dyes. The following changes in heavy metals concentrations in wastewater were found:

Cu	influent	0.003 - 0.005 mg/dm^3
	effluent	0.004 - 0.010 mg/dm^3
Zn	influent	0.007 - 0.027 mg/dm^3
	effluent	0.004 - 0.006 mg/dm^3



Rys 49. Zmiany zawartości azotu amonowego w procesie osadu czynnego.
Figure 49. Ammonia nitrogen changes in the activated sludge process.

Cr influent	0.005 - 0.015	mg/dm^3
effluent	0.002 - 0.014	mg/dm^3
Pb influent	0.018 - 0.036	mg/dm^3
effluent	0.021 - 0.023	mg/dm^3

Recapitulating the investigation results of wastewater treatment by the activated sludge method, it can be ascertained that this method is entirely useful. The activated sludge process enables efficient organic matter removal. However, this process does not effectively remove the color. The best color removal was not better than 30 percent.

6.2 THE ANAEROBIC DIGESTION OF WASTEWATER

Methodology and the Scope of Studies

A mixture of the municipal wastewater and digested sludge was basically applied in the test investigations.

The seven wastewater mixtures, described previously in the chapter on activated sludge process, have been applied.

The tests were conducted in the three sequential series:

Ist series employed: 20 cm^3 dose of mixture - daily discharged and and fed; 7-day detention time.

IInd series employed: 20 cm^3 dose of given mixture - daily fed; 7-day detention time.

IIIrd series consisted in the digestion without wastewater dosage; 7-day detention time.

The studies were accomplished by use of units of 200 ml mixed liquor volume. The initial mixed liquor for the Ist series was combined from 75 percent by volume of wastewater and 25 percent by volume of digested sludge. The digester final effluent obtained in the Ist series was used as feed material for the IInd series. Consequently, the final effluent from the IInd series was utilized as feed material in the IIIrd series.

The temperature of the process was 32 °C $\pm$ 1 °C.

The analytical control of the wastewater anaerobic digestion process involved the measurements of the quantity of gas, the pH value, the alkalinity, and the ammonia nitrogen concentration in the samples taken from the sludge digestion chamber after 7, 14 and 21 days.

Discussion of the Results

The investigation results indicated a relatively low ability of the tested wastewater to digestion. The quantity of gas produced in the course of the three series ranged in the limit of the measurement error. The systematic

drop in pH and alkalinity of wastewater during the digestion indicates an acid fermentation process. The pH and alkalinity changes in wastewater during the digestion process are shown in Figures 50 and 51.

A reduction in COD and color values of 10-19 percent and 4-10 percent, respectively, were obtained during the digestion process of wastewater employing the 7-day detention time.

Methodology and the Scope of Studies

The studies were carried out using two anaerobic bed units of different size. In the initial phase of studies, an anaerobic filter of 7.0 cm diameter and 180 cm height was used. The filter was filled with gravel of 2.5 to 3.5 cm graining. The total capacity of the filter was of 6.93 dm^3, and the empty space (not filled with gravel) was of 3.30 dm^3 capacity.

In the next phase of studies, a column of 14 cm in diameter and 250 cm in height was used.

The total volume of the anaerobic bed was of 38.5 dm^3, and the active volume of the bed was of 16.0 dm^3. The treated wastes under anaerobic conditions were then delivered to the aeration tank of the activated sludge process. The diagram of the applied experimental units is shown in Fig. 52.

The wastewater discharged by the anaerobic bed passed a tee unit in which a separation of the fermentation gas from the wastewater took place. The wastewater flowed off to a collecting vessel or to the next aerobic treatment phase. Whereas the gas was collected in a graduated glass tube displacing the wastewater from it.

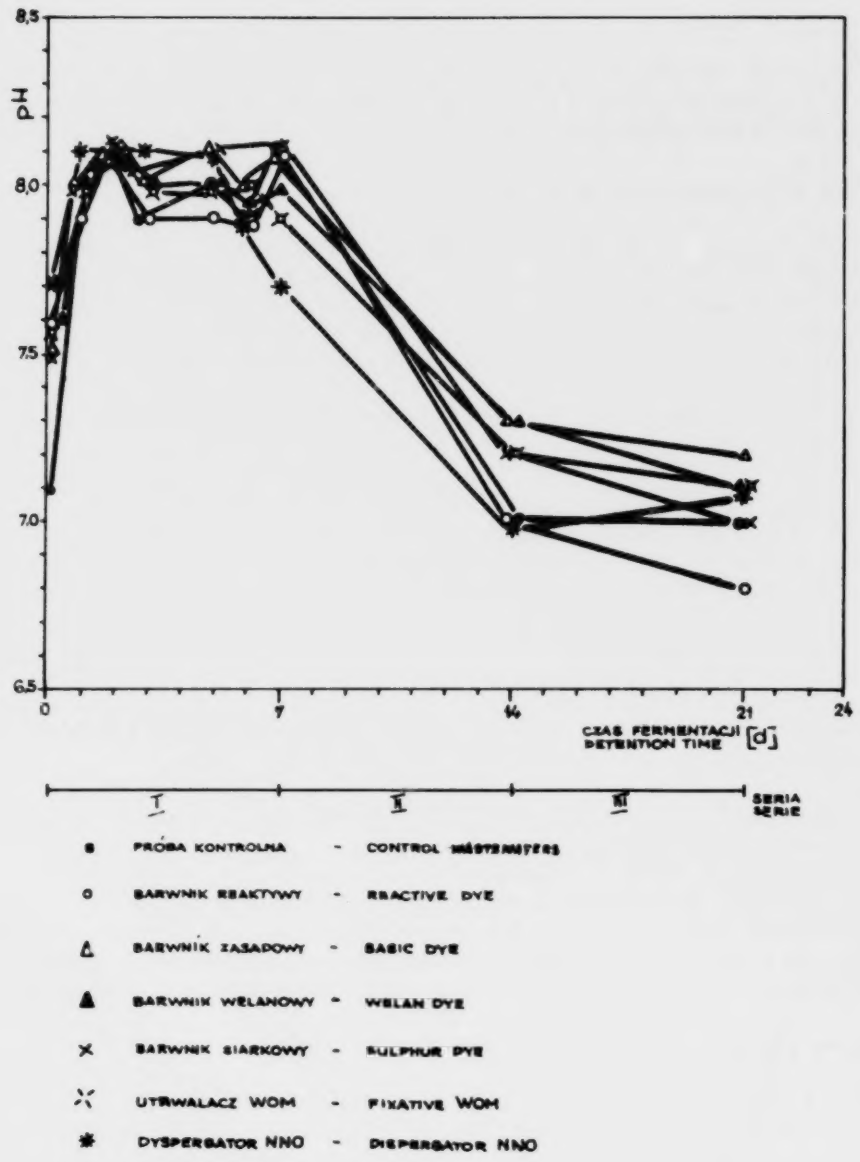
The anaerobic bed unit must be blacked out when the unit is constructed from a transparent material, i.e., metalplex.

The municipal wastewater with an addition of active dye Lunasol Rot 5B in the amount of 150 mg/dm^3 was the substrate used. An intensive red color was the feature of this mixture. In the second part of the studies, a 0.1 percent solution of dye bath on a municipal wastewater basis was used.

The Treatment Efficiency in Anaerobic Conditions

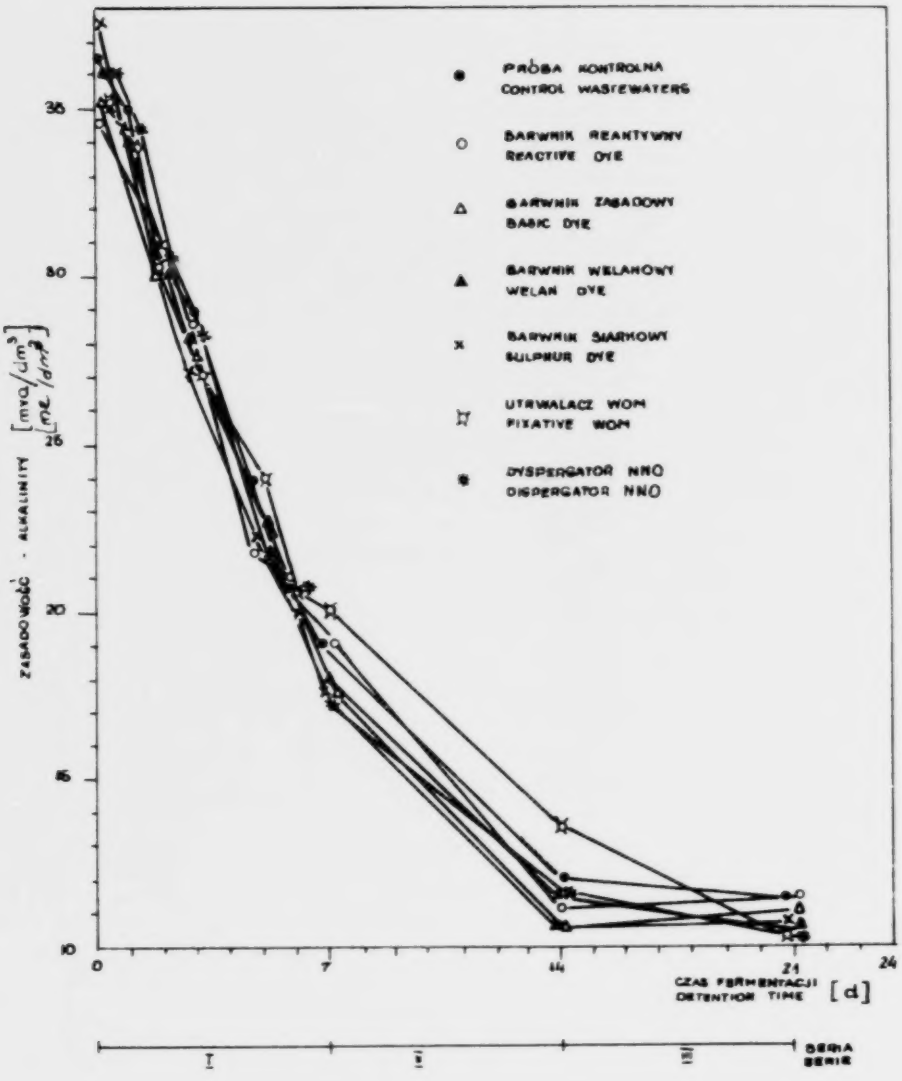
Despite the low concentrations of wastewater led to the anaerobic bed and subsequently short detention time of wastewater, very good removal of the organic matter was achieved. A 58 percent COD removal was obtained from a composition of municipal wastewater and the active dye of 310 mg/dm^3 COD concentration and at 3.5 day detention time. It should be emphasized that the anaerobic bed loading was only 0.089 kg $COD/m^3.d$. See Fig. 53.

For a much less loading of 0.035 kg $COD/m^3.d$ caused by a lower concentration of wastewater mixture and a longer detention time, the obtained removal of COD was only about 30 percent (Fig. 54).



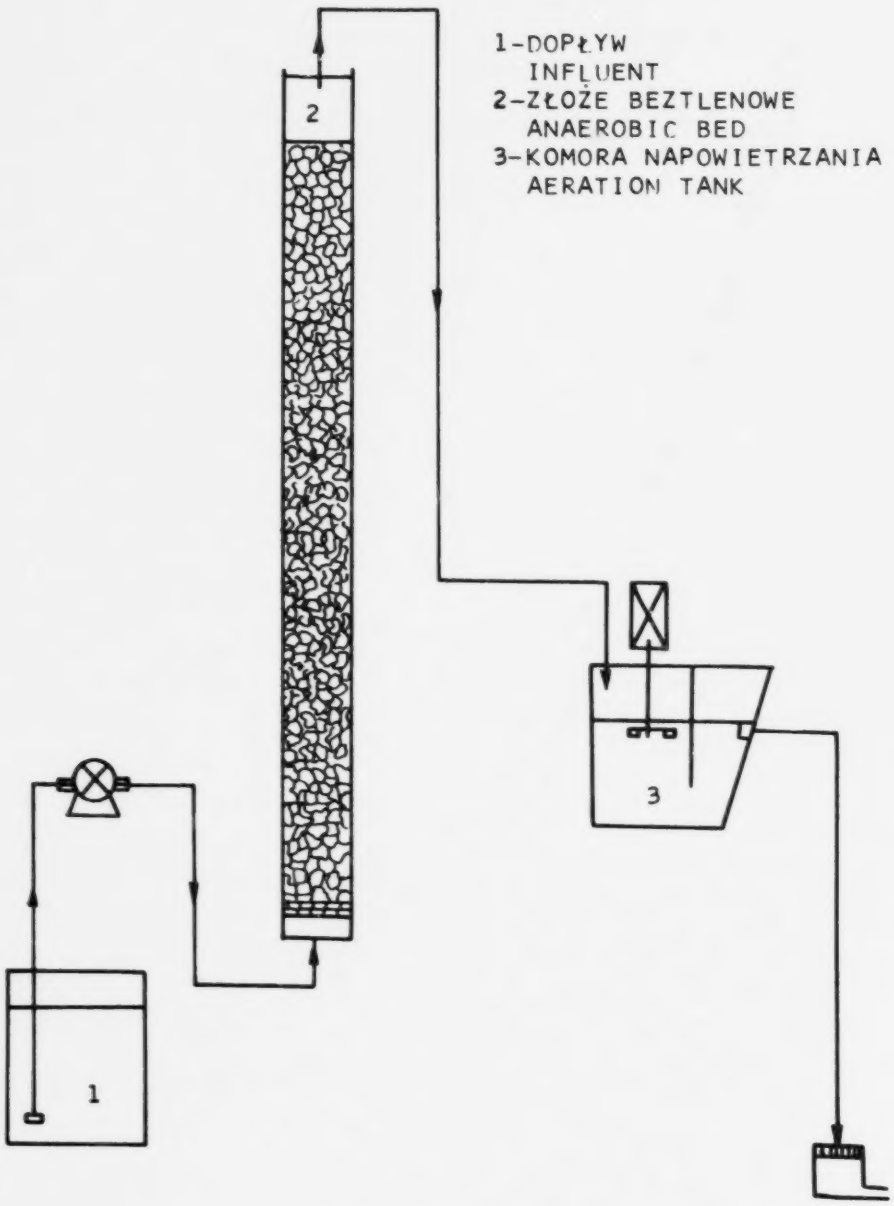
Rys 50. Zmizny pH w procesie beztlenowej fermentacji ścieków miejskich z dodatkiem wybranych barwnikow

Figure 50. Changes of pH values in the anaerobic treatment process of municipal wastewaters with addition of selected dyes

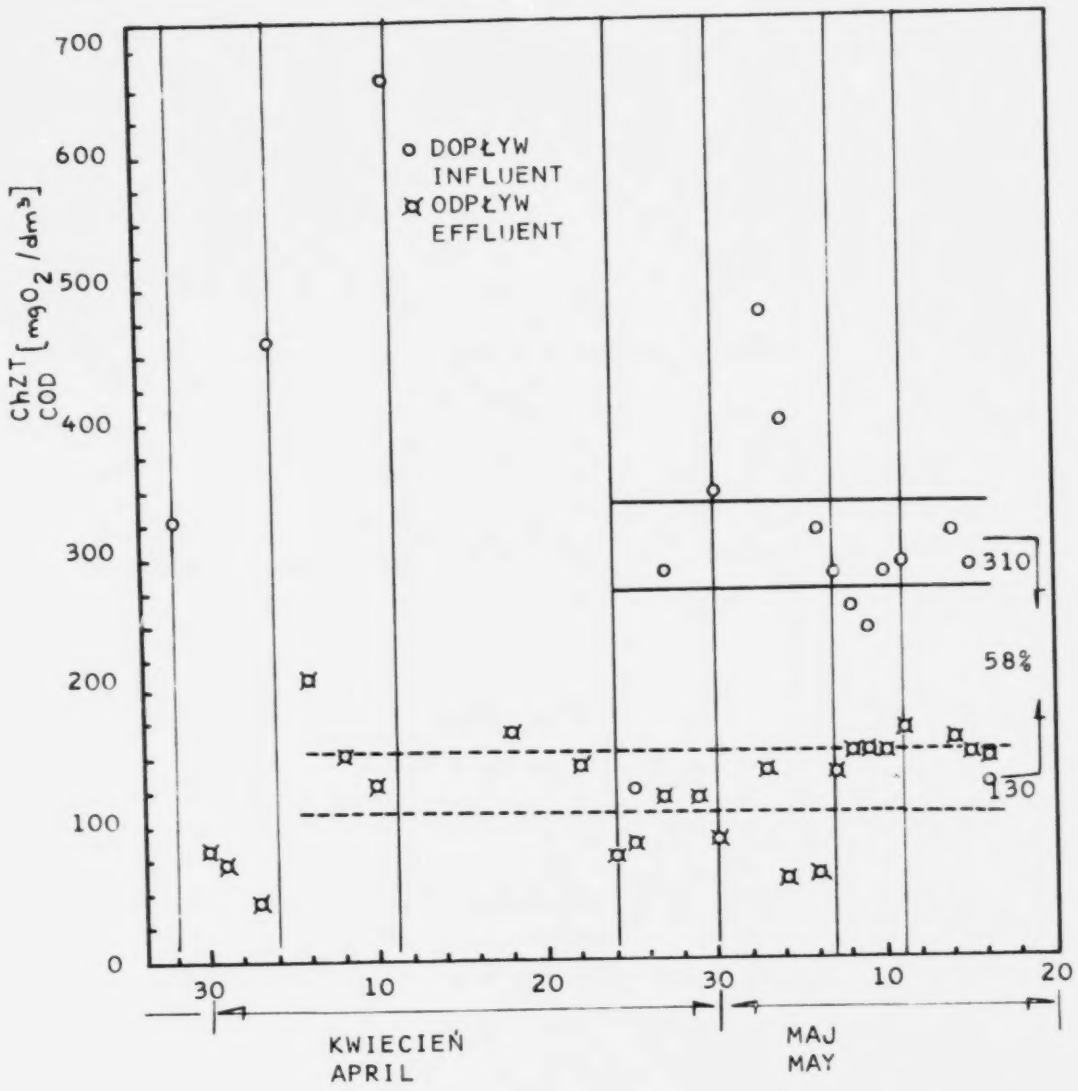


Rys 51. Zmiana zasadowości ścieków w procesie beztlenowej fermentacji ścieków miejskich z dodatkiem wybranych barwników.

Figure 51. Changes of alkalinity in the anaerobic treatment process of municipal wastewaters with addition of selected dyes.

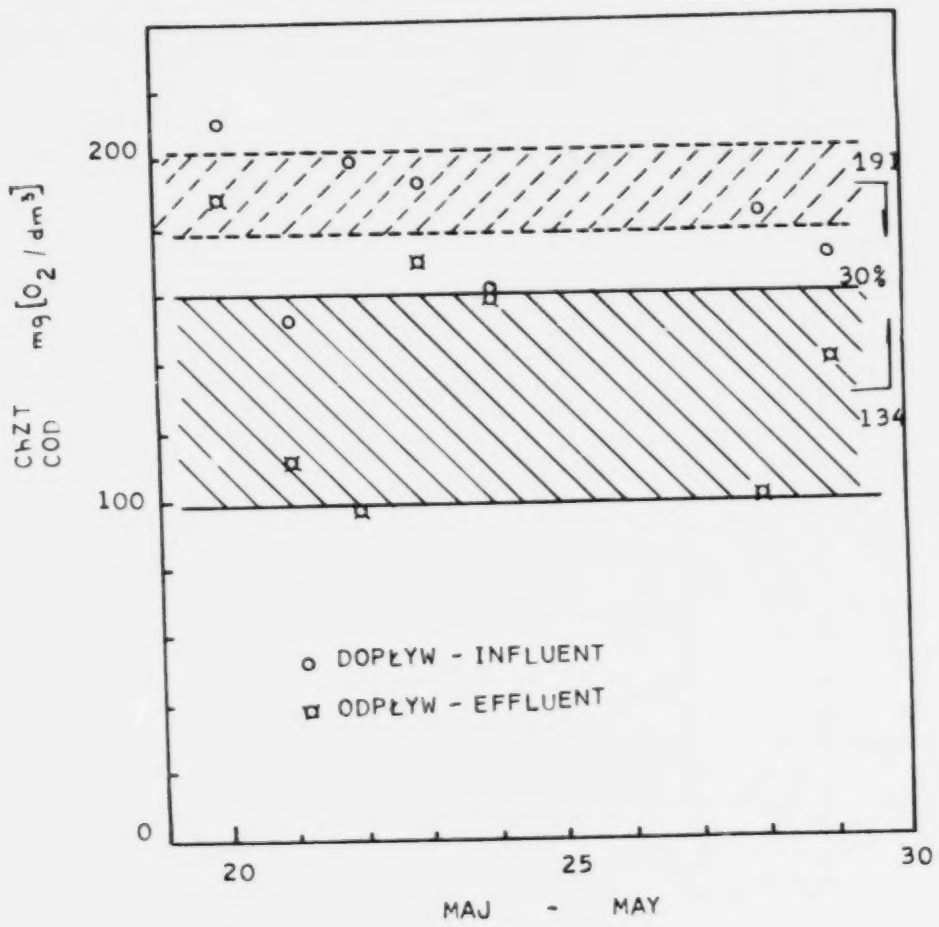


Rys 52. Schemat urządzeń doświadczalnych.
Figure 52. Laboratory equipment used for continuous studies on anaerobic and aerobic wastewaters treatment.



Rys 53. Efektywność usunięcia ChZT przy obciążeniu złoża ładunkiem 0.089 kg/m^3·d.

Figure 53. Efficiency of COD removal at the organic load of anaerobic bed equalled to 0.089 kg/m^3·d.



Rys 54. Efektywność usuniecia ChZT przy obciążeniu złoża ładunkiem 0.035 kg/m^3·d

Figure 54. Efficiency of COD removal at the organic load of anaerobic bed equalled to 0.035 kg/m^3·d.

An analysis of the other parameters of wastewater digestion process revealed a probability of a toxic interaction of active dye.

Similar COD removals were obtained in further studies with application of 0.1 percent dyeing wastewater solutions and at a lower load. For the wastewater mixture with a COD in a range of only 150-160 mg/dm^3 and at 8.42 day detention time in an anaerobic bed, the bed loading was 0.018 kg $COD/m^3 \cdot d$. At such low bed loading, a 31 percent and 17 percent COD removal were obtained. See Fig. 55.

The proceeding efficiency of wastewater methane fermentation became explicit when observing the increase in ammonia nitrogen concentrations. The ammonia nitrogen concentration in the wastewater introduced to the anaerobic bed was 29 mg/dm^3, while in the wastewater after treating on the bed, the ammonia nitrogen concentration increased to about 50 mg/dm^3 (Fig. 56). The increase was not a result of a change in the mineral nitrogen form, namely of a reduction of the oxidizable nitrogen form, but a consequence of biochemical degradation of organic substances. The organic nitrogen released from the organic matter could cause such significant increase in ammonia nitrogen concentration.

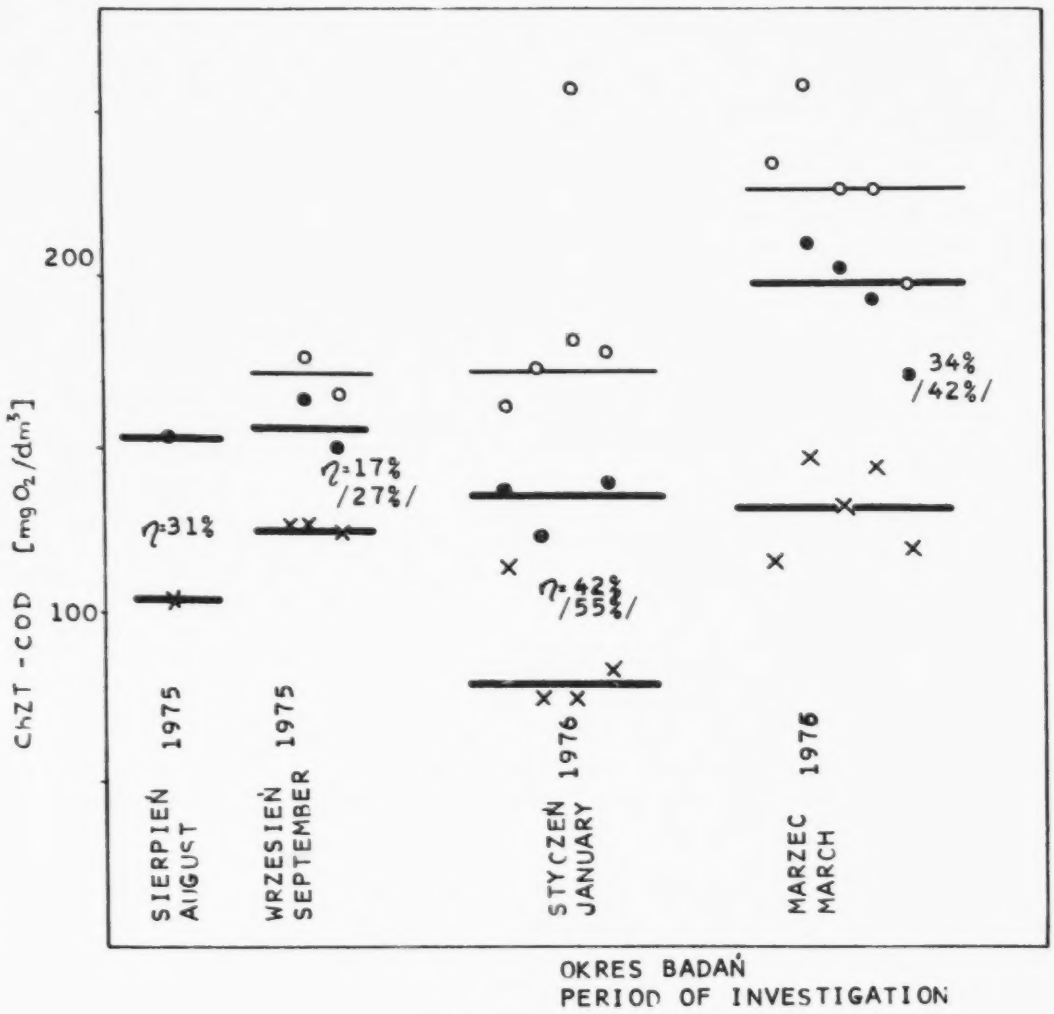
Subsequently with the ammonia nitrogen concentration increase, an increase in alkalinity of wastewater during the digestion process was observed. An average increase from 4.9 to 7.6 me/dm^3 were noted. The alkalinity changes in wastewater under anaerobic conditions and at a given testing period are presented in Fig. 57.

An unexpected removal intensification of COD was gained when increasing the hydraulic load to 0.256 $m^3/m^3 \cdot d$, and hence increasing the COD load to 0.0346 $g/dm^3 \cdot d$ as well as shortening the wastewater detention time to 3.90 days. The average COD removal determined from a filtered sample was 42 percent and 55 percent from the unfiltered sample treating the wastewater at the mentioned parameters (Fig. 55).

For the municipal wastewater of a higher concentration of organic substances, the anaerobic filter loading was 0.0556 $g/dm^3 \cdot d$, and the obtained COD removal efficiency was 34 percent for a filtered sample and 42 percent for unfiltered sample.

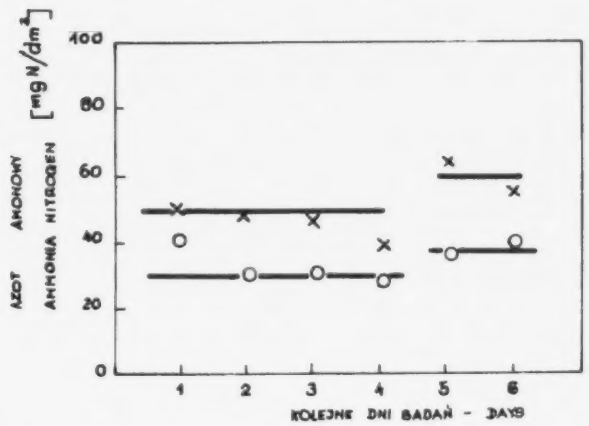
From the investigations carried out so far, a direct relationship between the wastewater treatment efficiency at anaerobic conditions and the hydraulic loading or pollution load was not found.

Considerable color removal was the most significant effect of anaerobic bed application to the textile wastewater treatment. The fresh discharge from the anaerobic bed was sometimes colorless or most often slightly colored and clear. Although in the contact with the air, it became turbid and gradually pink, but the final color intensity was far from the primary one. The process of the partial color reversion clearly appeared during the subsequent wastewater treatment using the activated sludge. Therefore, it seems to be reasonable to discuss the color removal effect from both the biological treatment stage aspects, i.e., anaerobic bed treating and the activated sludge



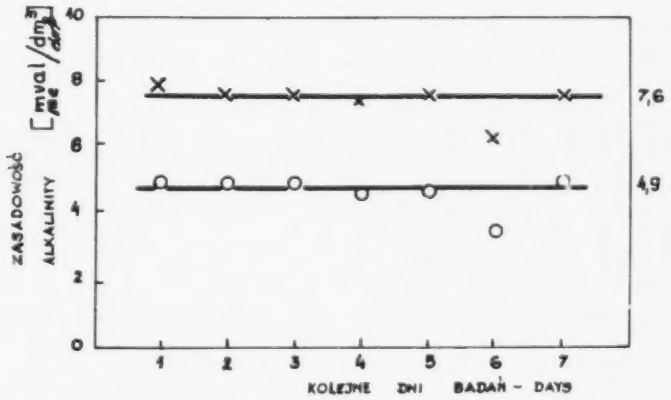
Rys 55. Zmiany ChZT sączonych próbek ścieków w procesie fermentacji w różnych okresach.

Figure 55. COD variations in the anaerobic wastewaters treatment appeared in different investigation periods.



× DOPŁYW - INFLUENT
○ ODPŁYW - EFFLUENT

Rys 56. Zmiany azotu amonowego w procesie fermentacji ścieków.
Figure 56. Changes of ammonia nitrogen in the anaerobic wastewater treatment.



× DOPŁYW - INFLUENT
○ ODPŁYW - EFFLUENT

Rys 57. Zmiany zasadowości ścieków w procesie ich fermentacji.
Figure 57. Changes of alkalinity in the anaerobic wastewater treatment.

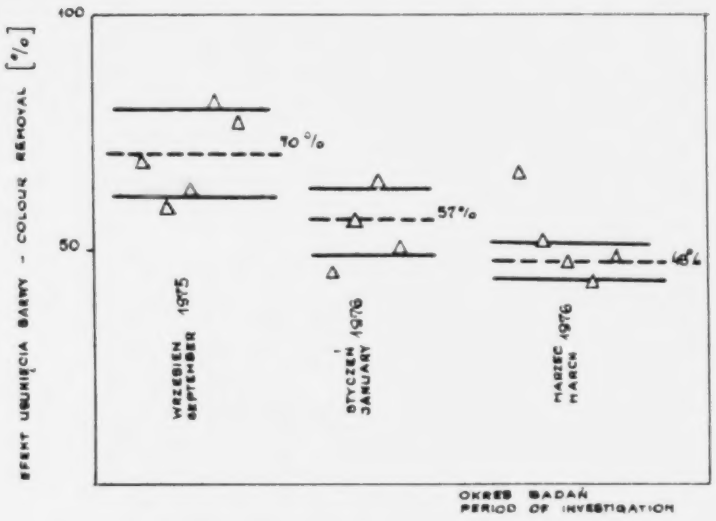
treating. Based on the investigation results, it can be stated that the activated sludge treatment method gives a 14 percent to 30 percent color reduction in the treated wastewater. The anaerobic bed application enabled a color reduction in the range of 49 percent to 82 percent, depending on the investigation period and the bed COD loading used. Figure 58 presents the results of the studies on color changes resulting from the two-stage process of biological treatment. The changes in color removal in correlation with the applied pollution loads can be approximately determined (Fig. 59). However, the relationship is not complete because it does not include the loading variations of the activated sludge. The existing suggestions, that the loading variability of activated sludge can be neglected, required a confirmation in the further studies. The main purpose of these studies was to prove the possibility of the partial chemical conversion of the complex organic substances during the anaerobic process. In the aerobic conditions, the organic substances are stabilized. The experience from these studies suggests that greater attention must be paid to the abilities and the usefulness of anaerobic processes in the wastewater treatment.

The dyeing wastewater treatment using only the activated sludge process produced an insignificant and sporadic color removal.

The above observations were confirmed by spectroscopic measurements in the visible and ultraviolet range using a UV-Vis Pye-Unicam 1800 model spectrophotometer with a spectrum recorder. The spectra were recorded in the full range or in a chosen range. Spectra examples of the crude and treated with sludge wastewater are presented in Fig. 60. These spectra performed during different periods of technological investigations revealed a lack of any conversions in the form of the investigated compounds. The different background values are merely due to the light diffusion caused by the presence of different suspended solids amounts or colloidal substances in the crude or treated wastewater.

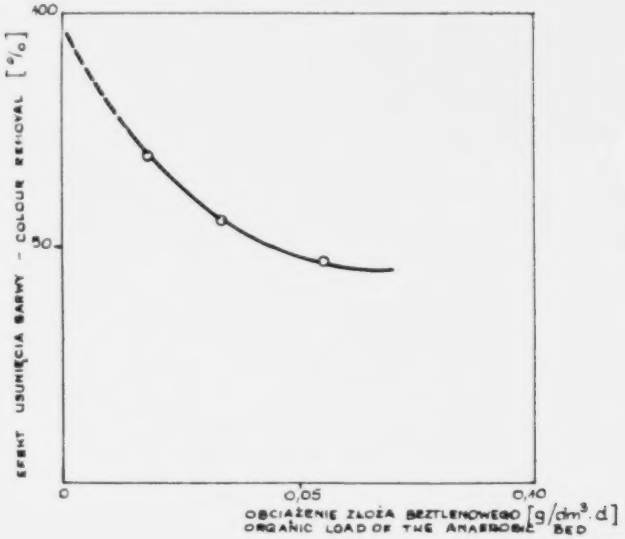
The color intensity was decreased by blending the dyeing bath and assistants with municipal wastewater. The dark color characteristic for such a mixture became changed with elapse of time. On the presented spectra, a point of inflection is observed at the 570 nm band. The resulting spectra changes due to the 5-days wastewater storage are shown in Fig. 61. A hypsochromatic shift of the absorption maximum appeared as well. A flocky sediment settling from the mixture of dyeing bath and municipal wastewater was observed. It can be suggested that a sorption phenomenon of dyes occurred on the organic suspended solids. However, the low rate of this phenomenon hints a more complex mechanism. It can be supposed as well that during the organic wastewater detention in the presence of bacterial microflora, biochemical and chemical processes take place. The biochemical processes were probably anaerobic. Subsequently, the suspended solids precipitation could result from the colloid stability shifting, as well as the carbonates forming in consequence of the solution pH value change.

The previously reported removal of color on the anaerobic bed prove that the course of phenomenon is of a biochemical mechanism. A spectrum of a strong adsorption band of range from 200-220 nm and a deflection point in 270 nm, was obtained for the dyeing wastewater solution on the influent to the



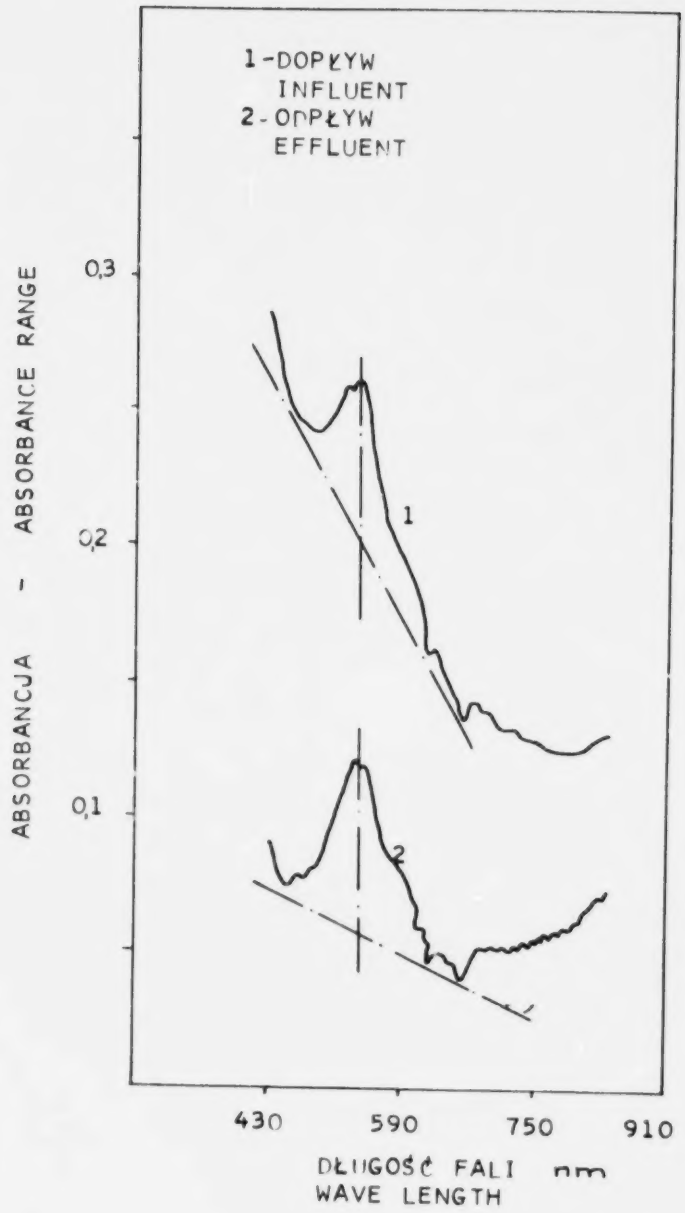
Rys 58. Zmiany efektywności usunięcia barwy w procesie fermentacji w różnych okresach badań.

Figure 58. Color removal variations in the anaerobic wastewater fermentation appeared in different investigation period.



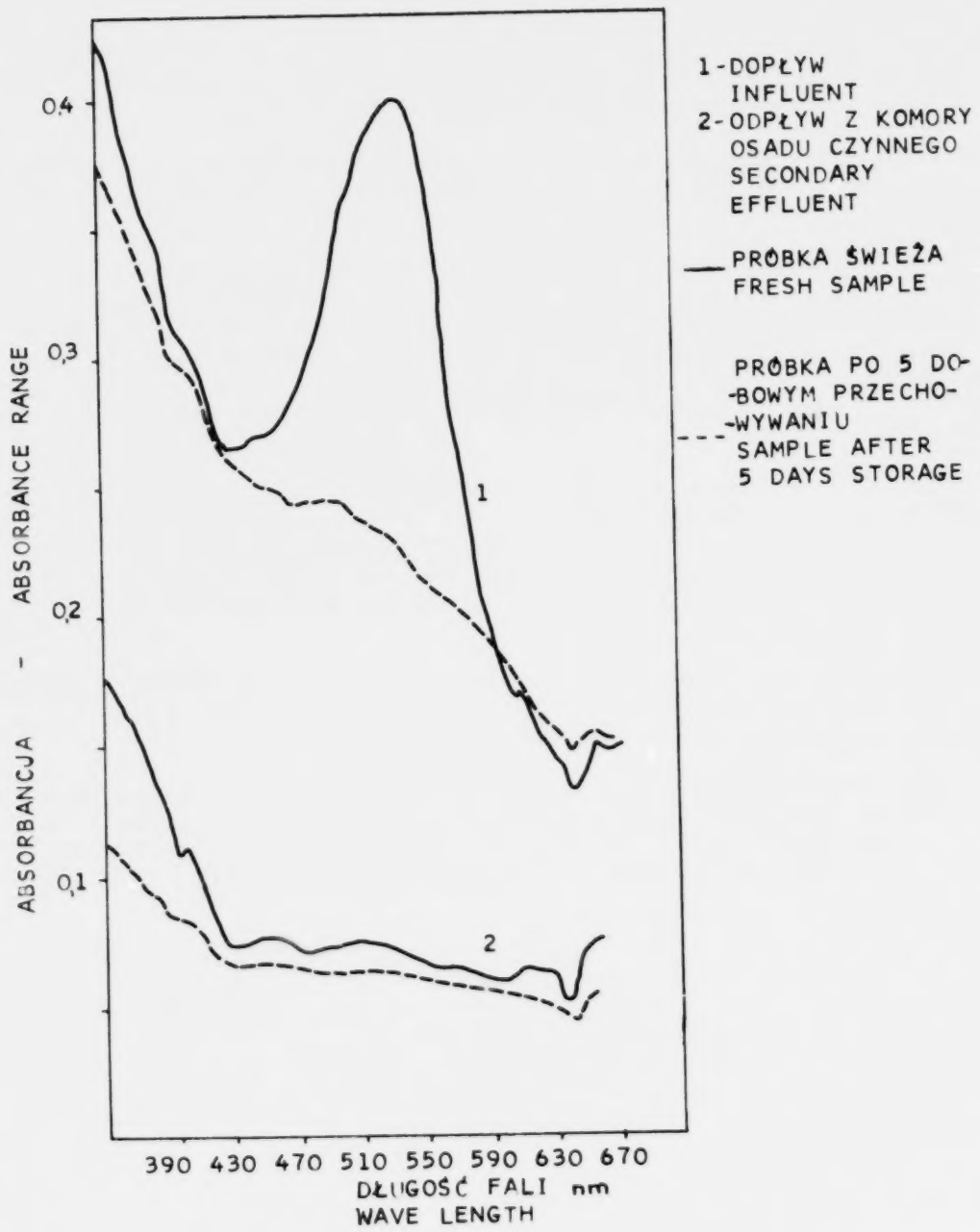
Rys 59. Zależność efektywności usunięcia barwy od obciążenia złoża beztlenowego ładunkiem ChZT.

Figure 59. Color removal in the anaerobic wastewater treatment effect of organic load of anaerobic bed expressed as g COD/dm^3.d.



Rys 60. Widma spektroskopowe ścieków przed i po oczyszczaniu osadem czynnym.

Figure 60. Spectra of the untreated and activated sludge treated wastewaters.



Rys 61. Zmiany widma ścieków w wyniku ich przechowywania.
Figure 61. Changes in wastewater spectra as a result of wastewater storage.

bed. A strong and wide adsorption band in the visible range of an adsorption maximum in 530 nm was seen also. The recorded spectrum for a solution diluted in the rate of 1:2.5, shown in Fig. 62, has a maximum in the 205 nm band. A similar spectrum shown in Fig. 63 has its maximum in the 206-220 nm band. The difference in the band of maximum location was likely the consequence of the differences between the municipal wastewater samples used.

The deflection point on the recorded spectra at the increased sensitivity (Fig. 64) or at the fourfold extended adsorption layer in a 4 cm cell appeared at the 410 nm band.

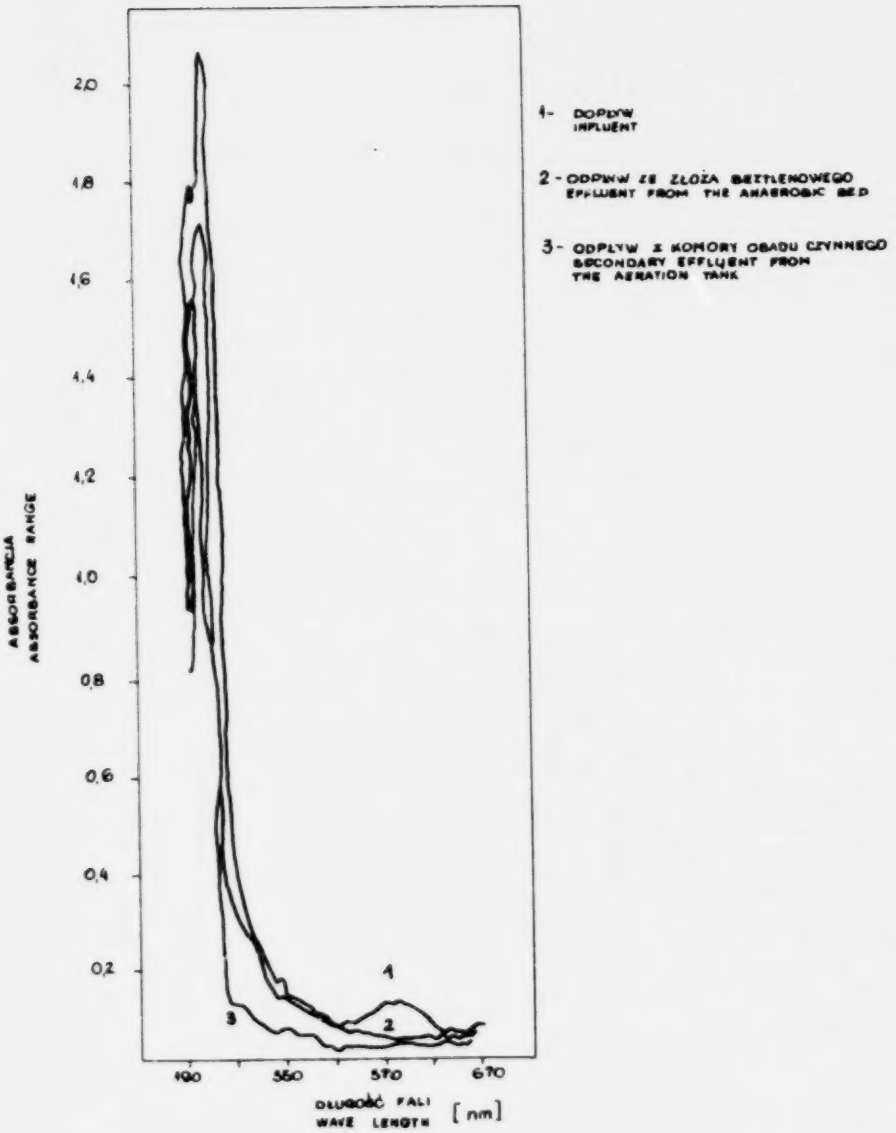
The fresh discharge from the anaerobic bed was transparent or very slightly colored and clear, but when stored in contact with the air, it became turbid and gradually pink colored; however, the final coloring changed little in comparison to the primary coloring. The spectra reveal a decrease in absorption maximum in the 530 nm (Fig. 62). In the ultraviolet range, there appears a second absorption maximum in the 350 nm band or a deflection point in the same band (Fig. 63).

In order to explain the color reversion phenomenon, the fresh discharge from the anaerobic bed was oxidized by use of the hydrogen peroxide solution. A momentaneous coloring increase was observed, which suggests that under anaerobic conditions a reduction occurs, producing a transient decolorizing. The oxidization results in a slight hypsochromic shifting of the absorption maximum.

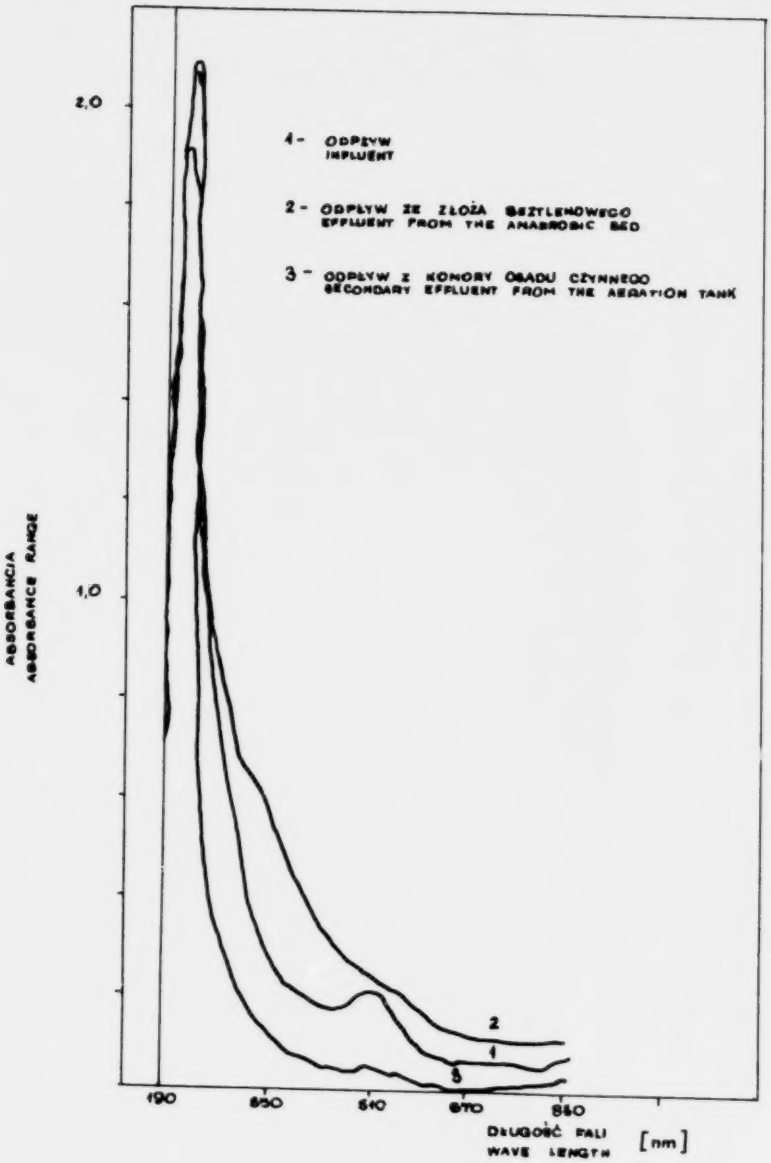
The activated sludge process in the second degree of treating, as was earlier mentioned, leads to a further color removal, in contrary to the separate application of the activated sludge treating method.

The differences between discharges from the anaerobic bed and the activated sludge tank become very apparent under the action of perchloric acid, which is shown in Fig. 65. The total and permanent decay of color appeared in the discharge from the tank, and the turbidity occurred in the discharge from the filter.

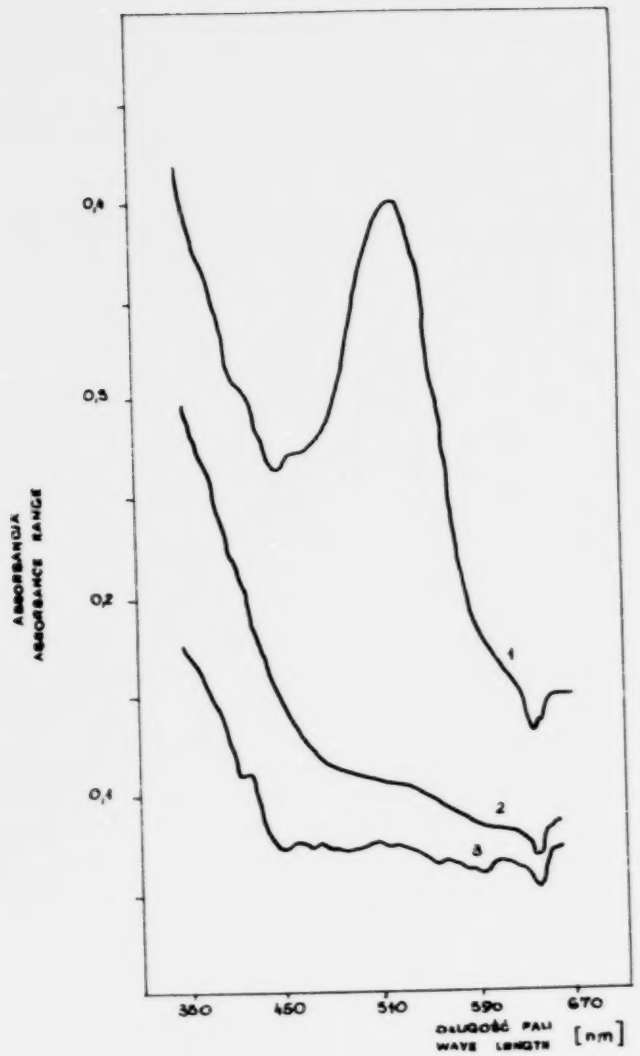
The color removal effect in a two-stage dyeing wastewater treatment was relatively high and the average equaled 75 percent (Fig. 66). Consequently, the two-stage treatment process application enabled the efficient removal of organic wastes expressed in terms of BOD_5 and COD. In the first treatment stage, a 37 percent COD removal, referred to the filtered samples, was gained. The joint COD removal in the two stages was of about 80 percent (Fig. 67). The changes in the other parameters expressed in concentrations are also presented in the same figure.



Rys 62. Zmiany widma ścieków w dwustopniowym procesie oczyszczania.
Figure 62. Changes in wastewater spectra in the anaerobic-aerobic wastewater treatment process.



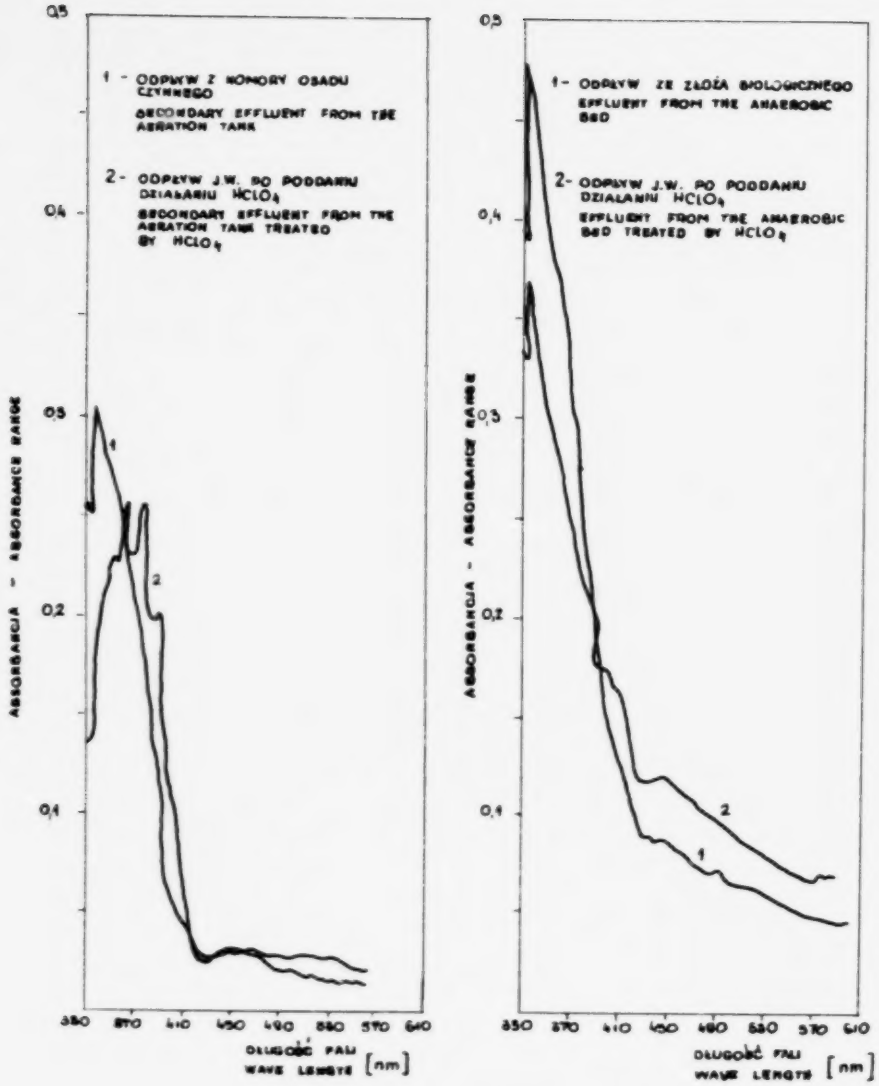
Rys 63. Zmiany widma ścieków w dwustopniowym procesie oczyszczania.
Figure 63. Changes in wastewater spectra in the anaerobic-aerobic wastewater treatment process.



1 - ODPŁYW - INFLUENT
2 - ODPŁYW ZE ZŁOŻA BEZTLENOWEGO - EFFLUENT FROM THE ANAEROBIC BED
3 - ODPŁYW Z KOMORY OSADU CZYNNEGO - SECONDARY EFFLUENT FROM THE AERATION TANK

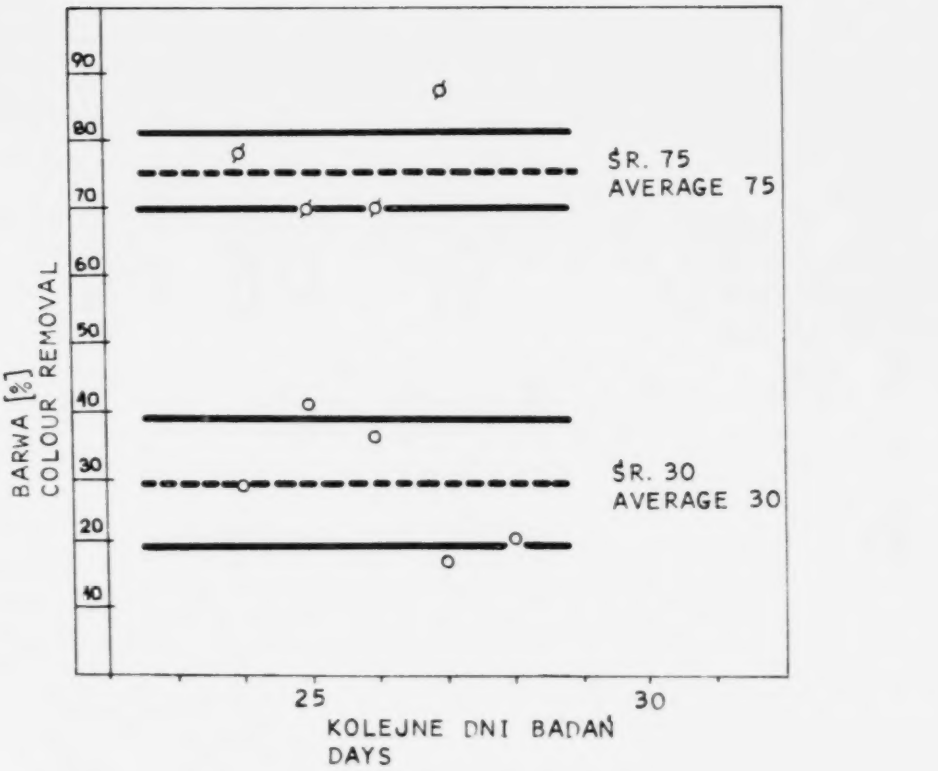
Rys 64. Wycinek widma ścieków biologicznie oczyszczonych, przy zwiększonej czułości.

Figure 64. Changes in spectra in visible range of wastewaters due to the biological method of treatment.


1 - ODPŁYW Z KOMORY OSADU CZYNNEGO
SECONDARY EFFLUENT FROM THE AERATION TANK
2 - ODPŁYW J.W. PO PODDANIU DZIAŁANIU $HClO_4$
SECONDARY EFFLUENT FROM THE AERATION TANK TREATED BY $HClO_4$
1 - ODPŁYW ZE ZŁOŻA BIOLOGICZNEGO
EFFLUENT FROM THE ANAEROBIC BED
2 - ODPŁYW J.W. PO PODDANIU DZIAŁANIU $HClO_4$
EFFLUENT FROM THE ANAEROBIC BED TREATED BY $HClO_4$
ABSORBANCJA - ABSORBANCE RANGE
0,5
0,4
0,3
0,2
0,1
350 370 410 450 490 530 570 610
DŁUGOŚĆ FALI WAVE LENGTH [nm]

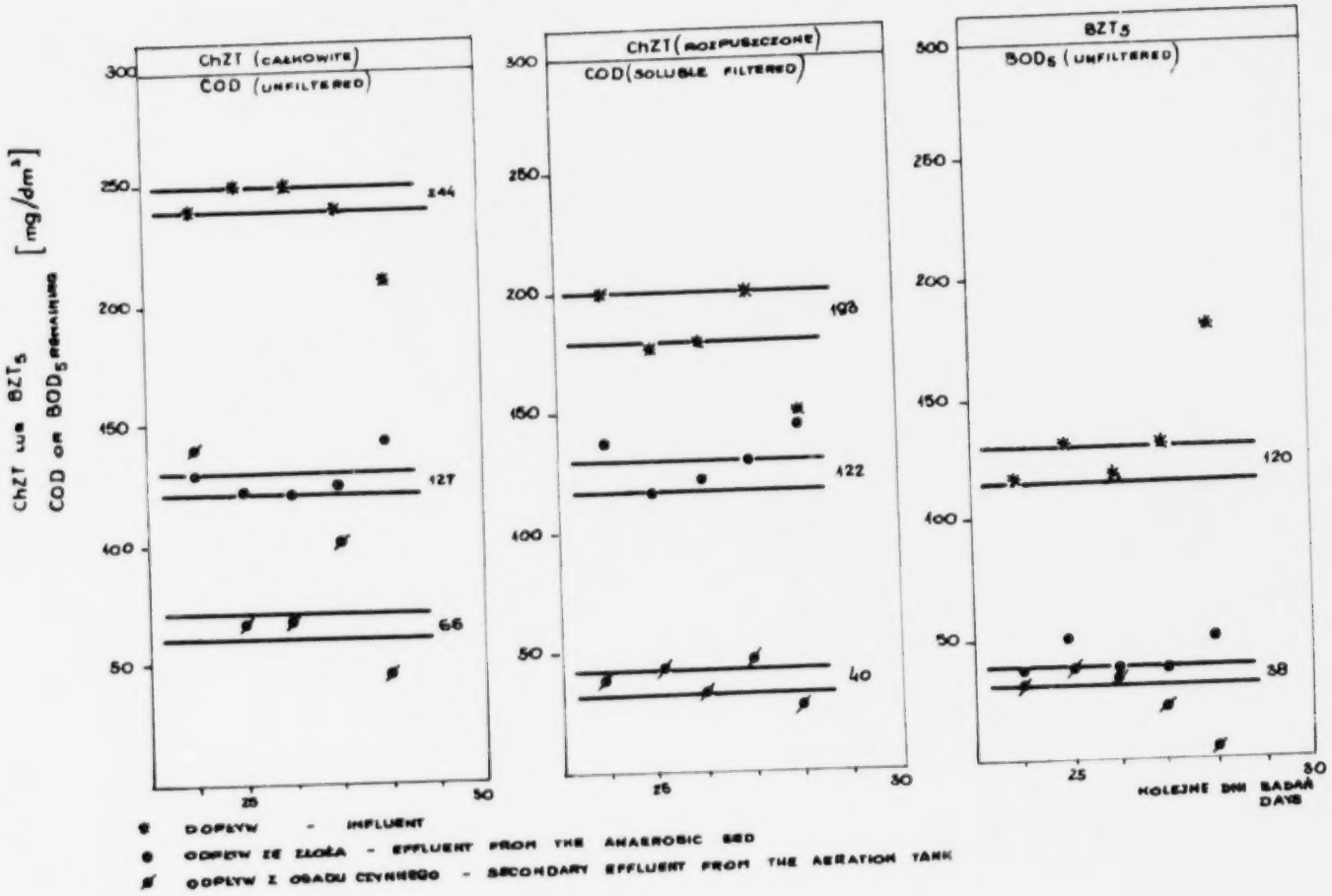
Rys 65. Zmiana widma ścieków poddanych działaniu kwasu nadchlorowego w zależności od stopnia ich oczyszczania.

Figure 65. Changes in wastewater spectra due to the biological method of treatment-effect of $HClO_4$ addition to the treated wastewater.



Rys 66. Efekty usunięcia barwy w dwustopniowym procesie oczyszczania ścieków.

Figure 66. Color removal by the anaerobic and aerobic wastewater treatment process.



Rys 67. Zmiany zawartości substancji organicznych w dwustopniowym procesie biologicznego oczyszczania.
Figure 67. Changes of organic substances concentration in the anaerobic and aerobic wastewater treatment process.

SECTION 7

THE INFLUENCE OF THE SELECTED CONTAMINANTS ON THE ANAEROBIC DIGESTION OF SLUDGE

The Scope and Methodology of Studies

The dye and assistants concentrations studied for the influence on the methane production are listed in Tables 13 and 4.

The investigations used laboratory digestion tanks of 610 cm^3 total capacity and a 400 cm^3 sludge volume. The digestion process was carried out at the constant sludge volume and at the temperature of 32 °C without sludge feeding. The digestion controls included the daily measurement of gas and the physical and chemical analysis of sludge. The data were taken after 0, 10, 20, and 41 or 45 days of digestion.

The physical and chemical analyses were carried out by the commonly accepted methods. The fatty acids contents in the oversludge liquid were determined by use of the gas chromatograph applying the Pye-Unicam Model 105 chromatograph. The separation was done in a column fed with 5 percent "F.F.A.P." phase settled on 101 chromosorp. The detection was conducted by use of a flame-ionizing detector. The chromatogram assessment was performed by comparing the chromatograms with fatty acids standard solutions, i.e., the acetic, propionic, butyric, isovaleric, and valeric acids.

The sludge mixture containing 60 percent by volume of primary settling tanks sludge and 40 percent by volume of digested sludges from the municipal wastewater treatment plants was the initial material for the studies.

The initial material contained from 26.7 to 38.8 g/cm^3 solid residue, and the volatile parts contents in sludge varied from 62 percent to 67.5 percent. The effect of the added substances on the sludge anaerobic digestion was evaluated by comparison of the produced quantity of gas, and physical and chemical analysis results of sludges for the tested and reference samples.

The Results of Studies

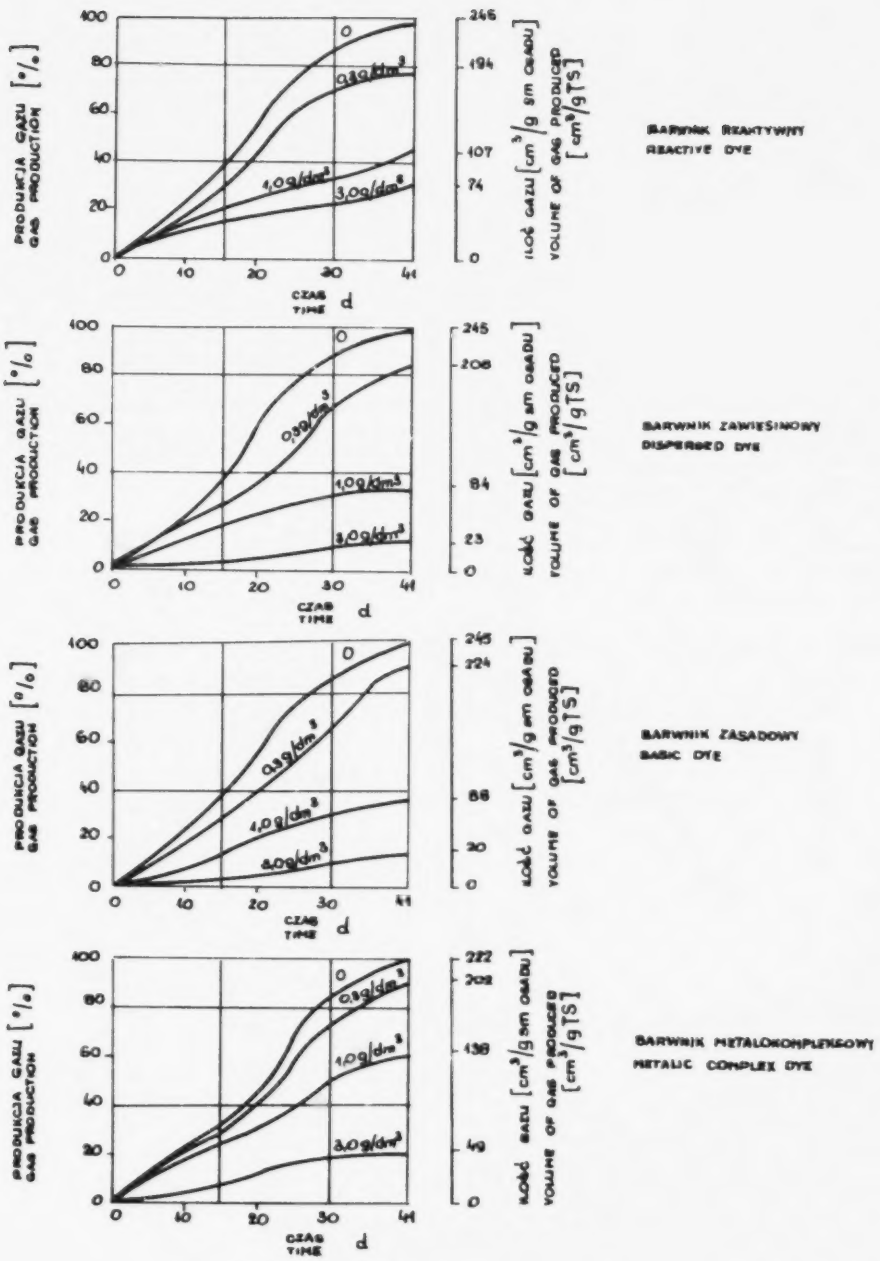
The investigation results enabled the determination of the concentration of the tested substances which inhibit the gas production in the digestion process. The results are shown in Figures 68 to 73.

The rate of the daily gas production in relationship with the concentrations of the chosen substances in sludges is shown in Figures 74 to 76.

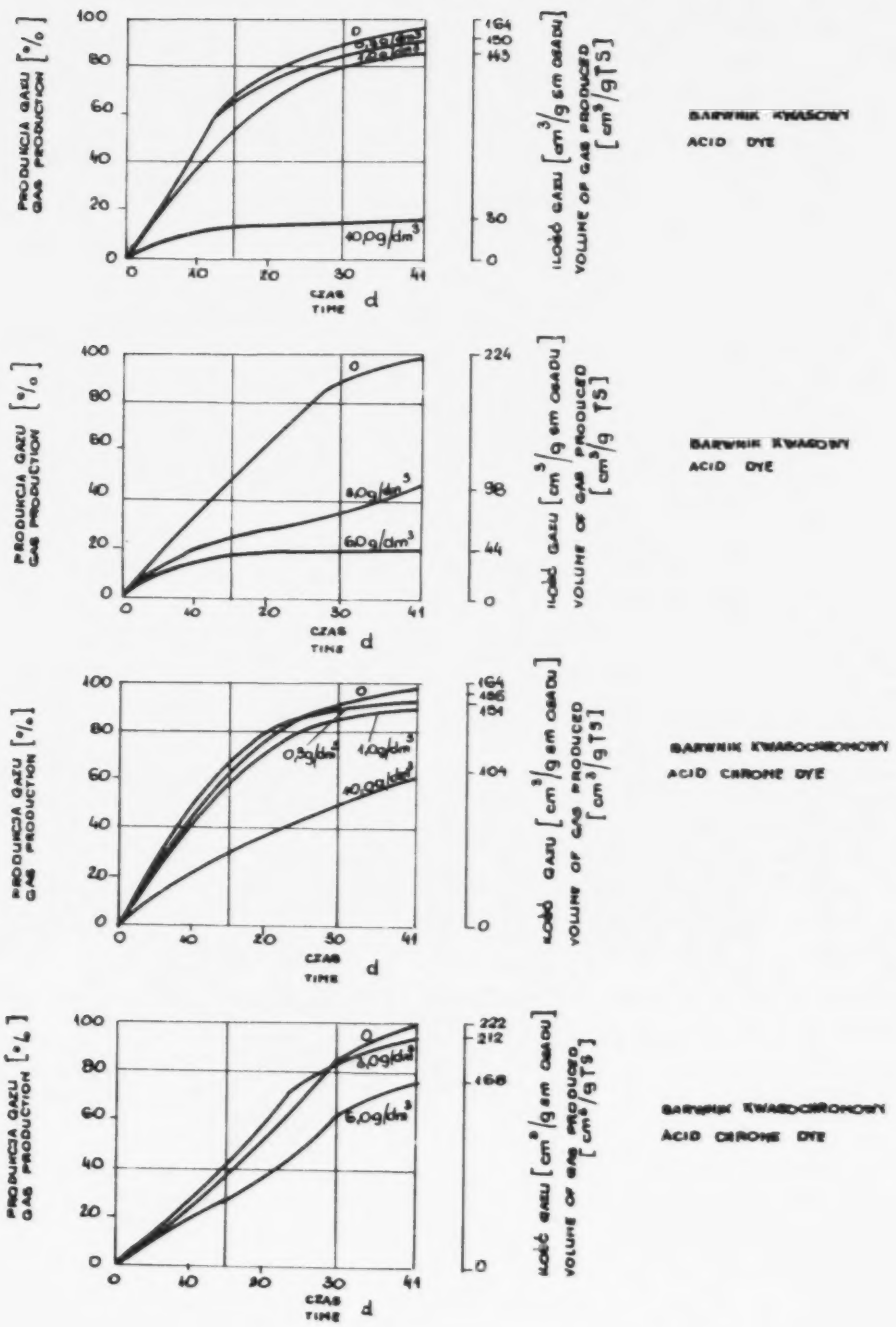
TABLE 13. CONCENTRATION RANGE OF THE TESTED SUBSTANCES

Type of dye or assistant	Series Number	Concentration, g/dm^3				
1. Active dye: lunasol rot 5B	III	0.3	1.0	3.0		
2. Dispersed dye: synthetic yellow	III	0.3	1.0	3.0		
3. Basic dye: aniline red BL	III	0.3	1.0	3.0		
4. Metal complex dye: polfalon green 2BL	III	0.3	1.0	3.0		
5. Direct dye: helion yellow	II	0.3	1.0			10.0
	III			3.0	6.0	
6. Acid dye: folan red B	II	0.3	1.0			10.0
folan red G	III			3.0	6.0	
7. Chrome dye: chrome red B	II	0.3	1.0			10.0
	III			3.0	6.0	
8. Sulfuric dye: sulfur brown	II	0.3	1.0			10.0
	III			3.0	6.0	
9. Welan dye: welan brown	II	0.3	1.0			10.0
10. Half-wool dye: strong red PGL	II	0.3	1.0			10.0
	III			3.0	6.0	
11. Assistant: fixing agent WOM	II	0.3	1.0			10.0
	III			3.0	6.0	
12. Assistant: dispersing agent NNO	II	0.3	1.0			10.0
13. Assistant: elanofor	II	0.3	1.0			10.0
14. Dyeing bath mixture[X]		0.3%		1.0%		5%

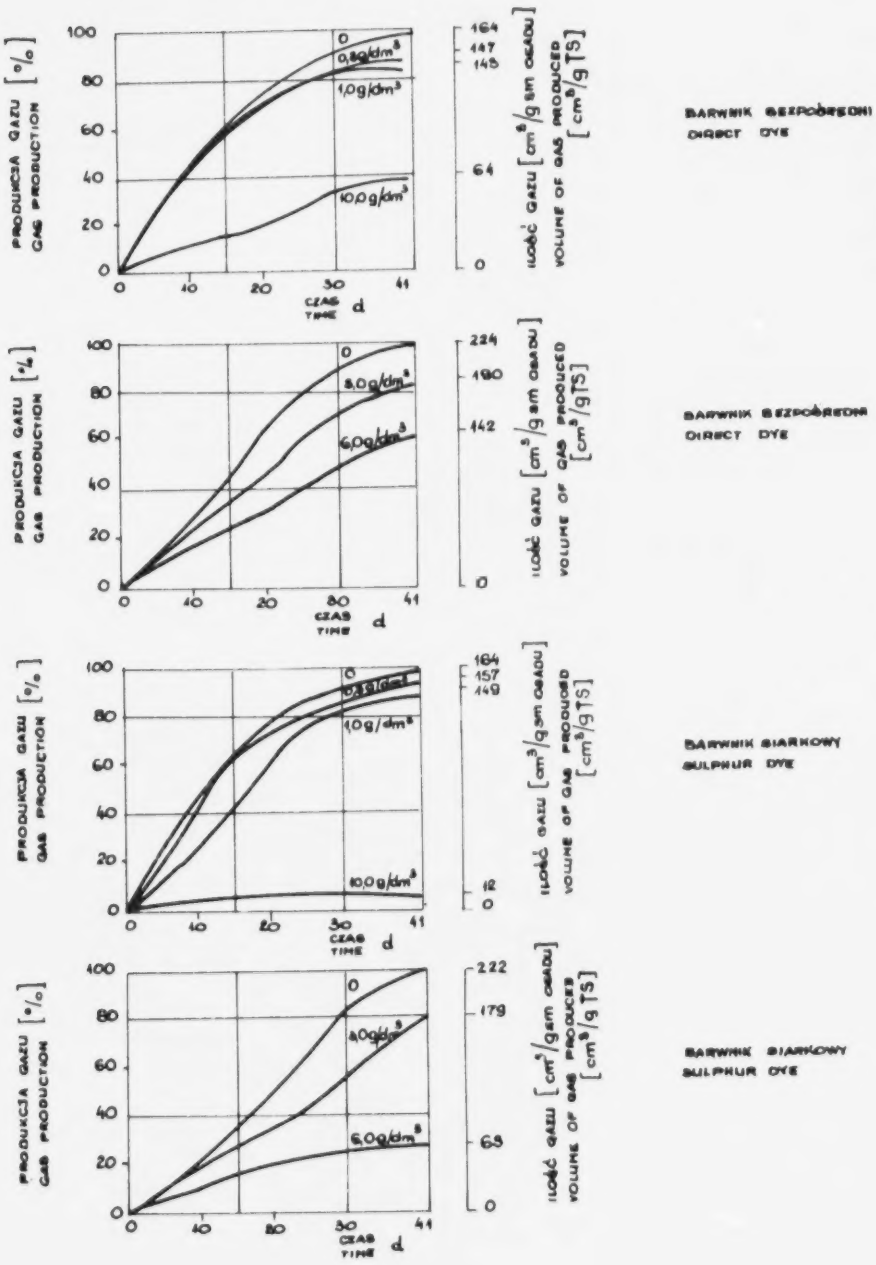
[X]Content is given in Table 4



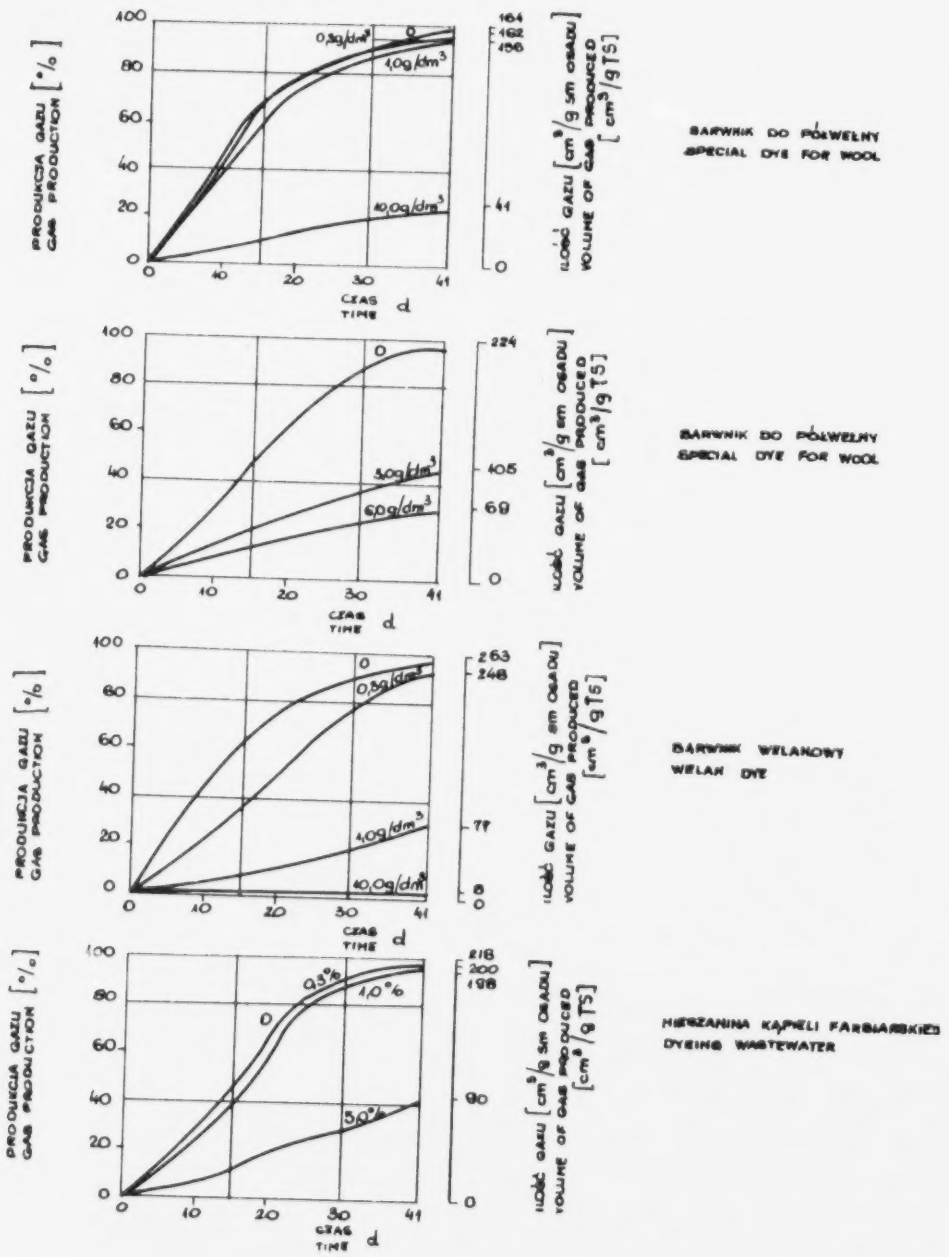
Rys 68. Produkcja gazu w procesie beztlenowej fermentacji osadów.
Figure 68. Gas production in the anaerobic sludge digestion.



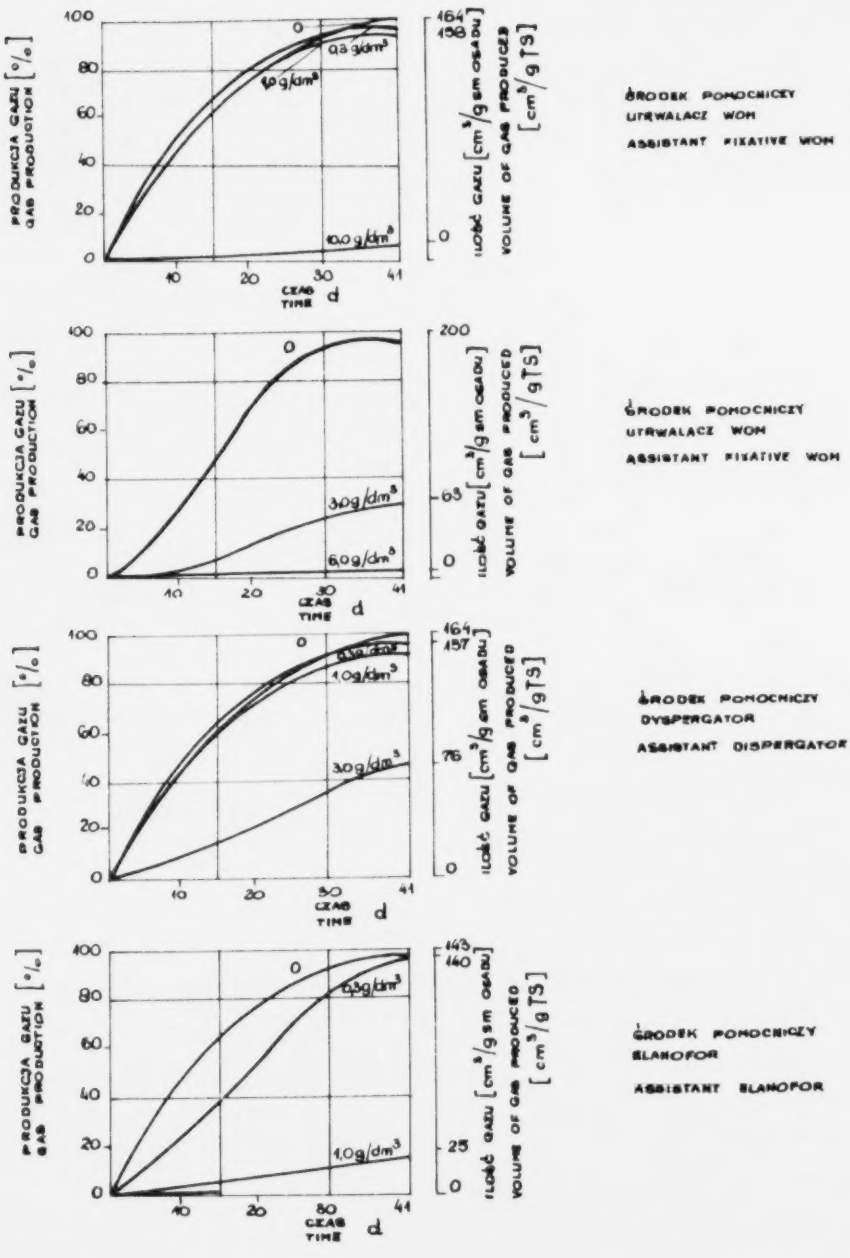
Rys 69. Produkcja gazu w procesie beztlenowej fermentacji osadów.
Figure 69. Gas production in the anaerobic sludge digestion.



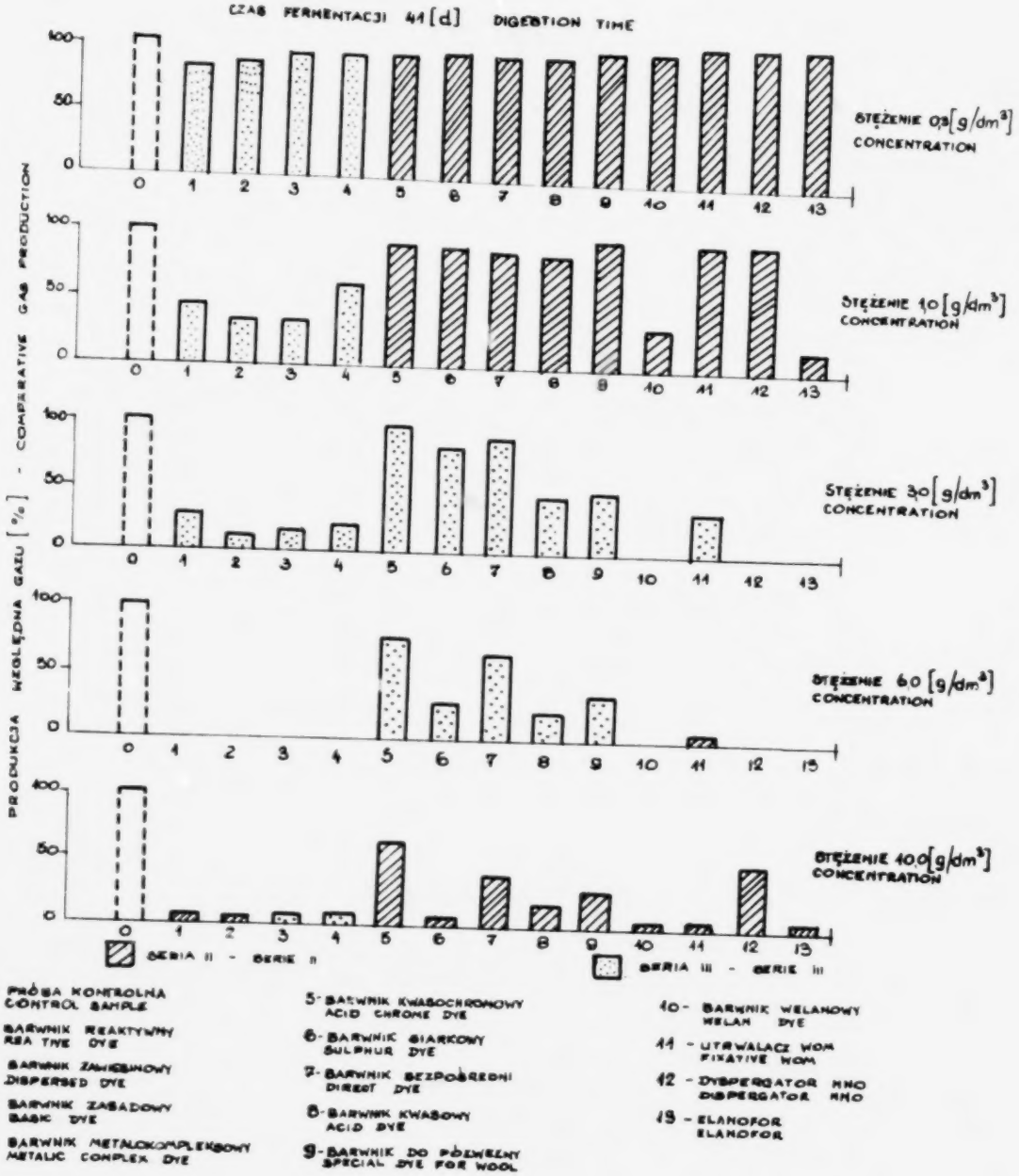
Rys 70. Produkcja gazu w procesie beztlenowej fermentacji osadów.
Figure 70. Gas production in the anaerobic sludge digestion.



Rys 71. Produkcja gazu w procesie beztlenowej fermentacji osadów.
Figure 71. Gas production in the anaerobic sludge digestion.

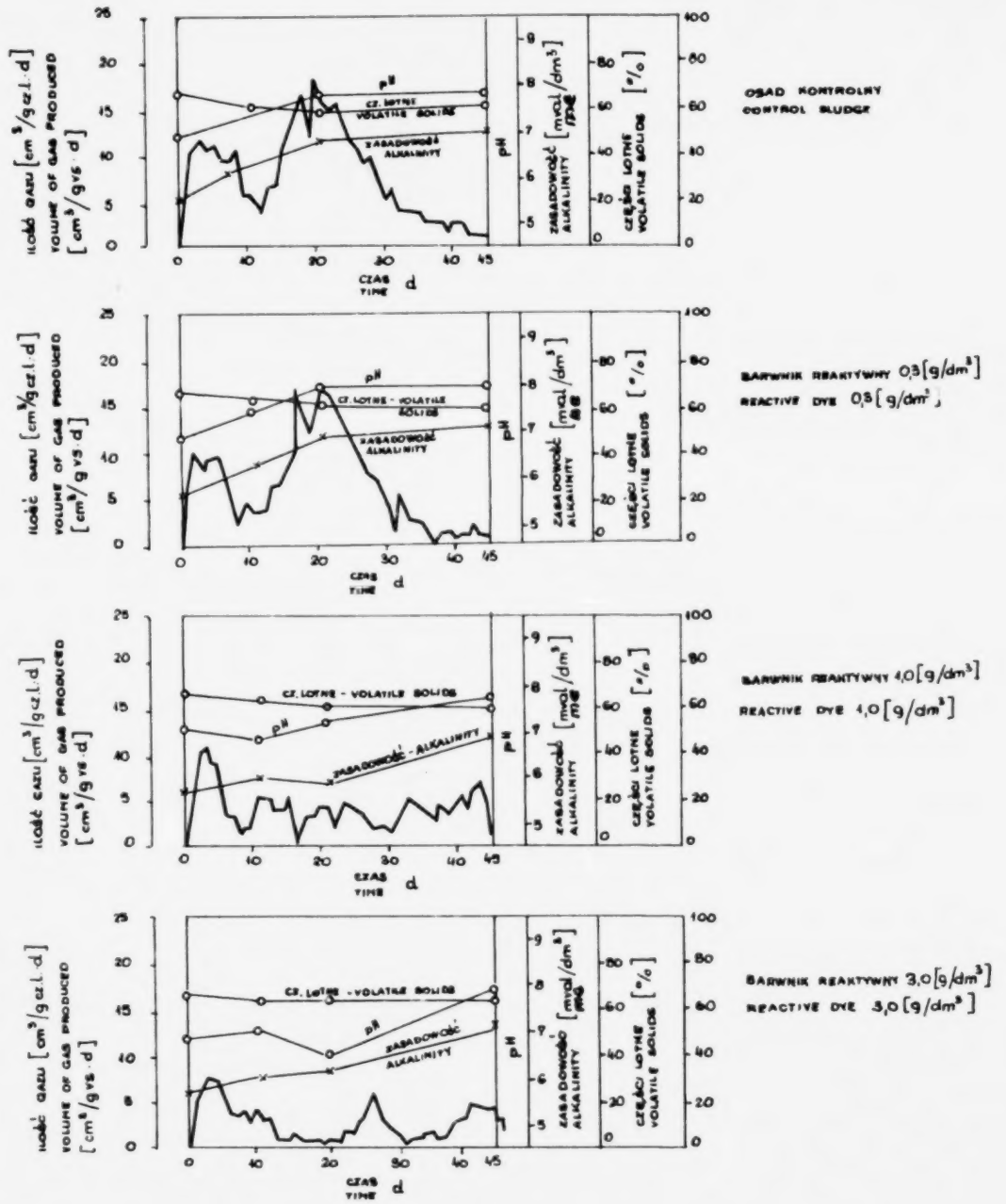


Rys 72. Produkcja gazu w procesie beztlenowej fermentacji osadów.
Figure 72. Gas production in the anaerobic sludge digestion

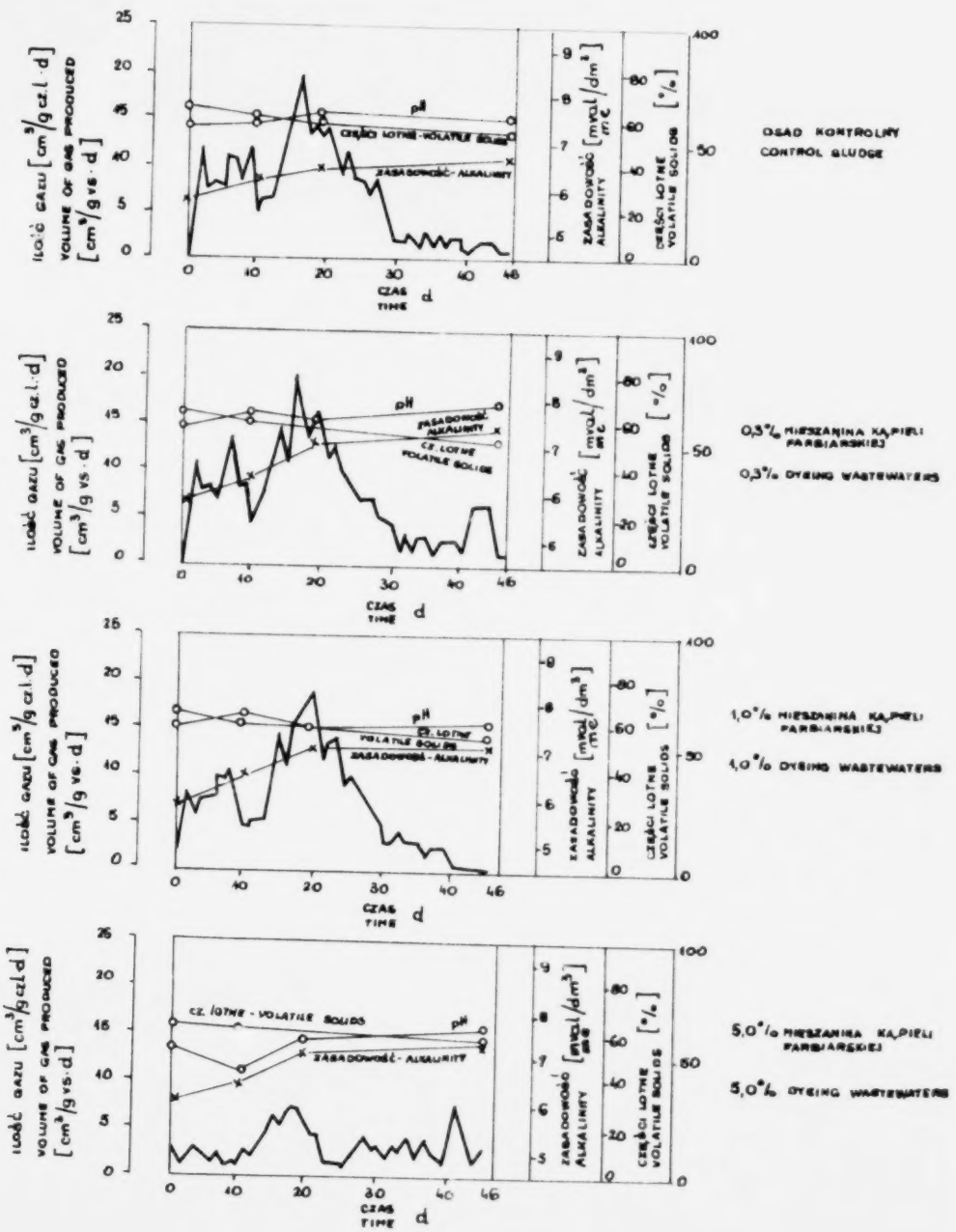

CZAS FERMENTACJI 44 [d] DIGESTION TIME
PRODUKCJA WZGLĘDNA GAZU [%] - COMPERATIVE GAS PRODUCTION
STĘŻENIE 03 [g/dm³] CONCENTRATION
STĘŻENIE 10 [g/dm³] CONCENTRATION
STĘŻENIE 30 [g/dm³] CONCENTRATION
STĘŻENIE 60 [g/dm³] CONCENTRATION
STĘŻENIE 100 [g/dm³] CONCENTRATION
SERIA II - SERIE II
SERIA III - SERIE III
0 - PRÓBA KONTROLNA CONTROL SAMPLE
1 - BARWNIK REAKTYWNY REA TIVE DYE
2 - BARWNIK ZAWIESINOWY DISPERSED DYE
3 - BARWNIK ZASADOWY BASIC DYE
4 - BARWNIK METALOKOMPLEKSOWY METALIC COMPLEX DYE
5 - BARWNIK KWASOCHROMOWY ACID CHROME DYE
6 - BARWNIK SIARKOWY SULPHUR DYE
7 - BARWNIK BEZPOŚREDNI DIRECT DYE
8 - BARWNIK KWASOWY ACID DYE
9 - BARWNIK DO PÓŁWEŁNY SPECIAL DYE FOR WOOL
10 - BARWNIK WEŁNOWY WOLAN DYE
11 - UTRWALACZ WOM FIXATIVE WOM
12 - DYSPERGATOR NNO DISPERGATOR NNO
13 - ELANOFOR ELANOFOR

Rys 73. Wpływ stężen barwników i srodków pomocniczych na produkcję, gazu w procesie beztlenowej fermentacji osadów.

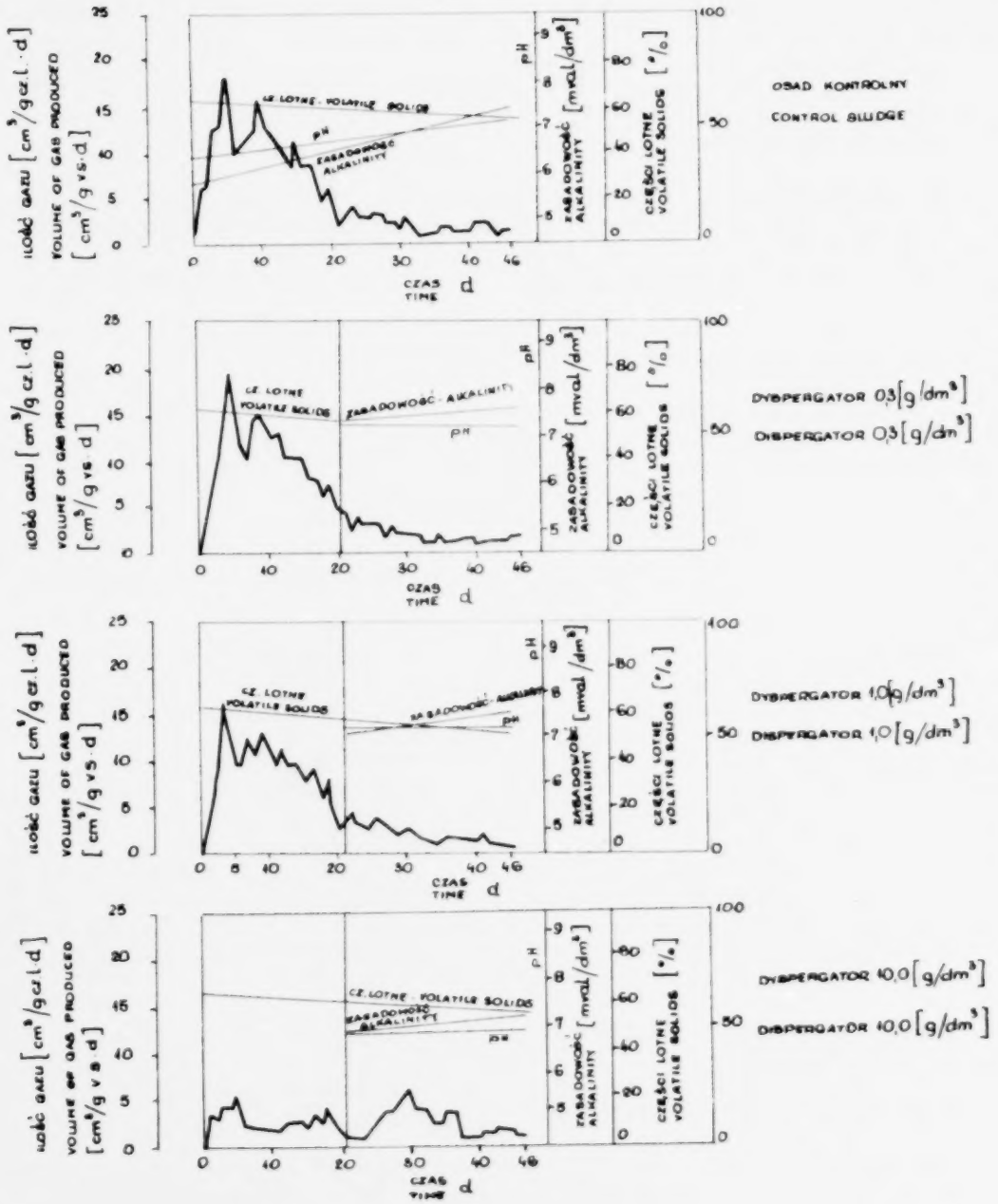
Figure 73. Gas production in the anaerobic sludge digestion effect of dyes and assistants concentration.



Rys 74. Szybkość produkcji gazu w procesie beztlenowej fermentacji osadów.
Figure 74. Gas production rate in the anaerobic sludge digestion.



Rys 75. Szybkość produkcji gazu w procesie beztlenowej fermentacji osadów.
Figure 75. Gas production rate in the anaerobic sludge digestion.



Rys 76. Szybkość produkoji gazu w procesie beztlenowej fermentacji osadów.
Figure 76. Gas production rate in the anaerobic sludge digestion.

This rate presents the influence of the tested substances on the digestion process.

Fig. 77 shows the concentrations of the free volatile fatty acids after about 10, 20, and 45 days of sludge digestion, containing an addition of separate dyes and assistants.

The investigations revealed that the 300 mg/dm^3 concentration of separate dyes in sludges did not appreciably affect the sludge methane digestion process. The gas production in conversion on 1 g of the sludge solid mass after 41 days digestion was about 10 percent reduced in relation to the reference samples.

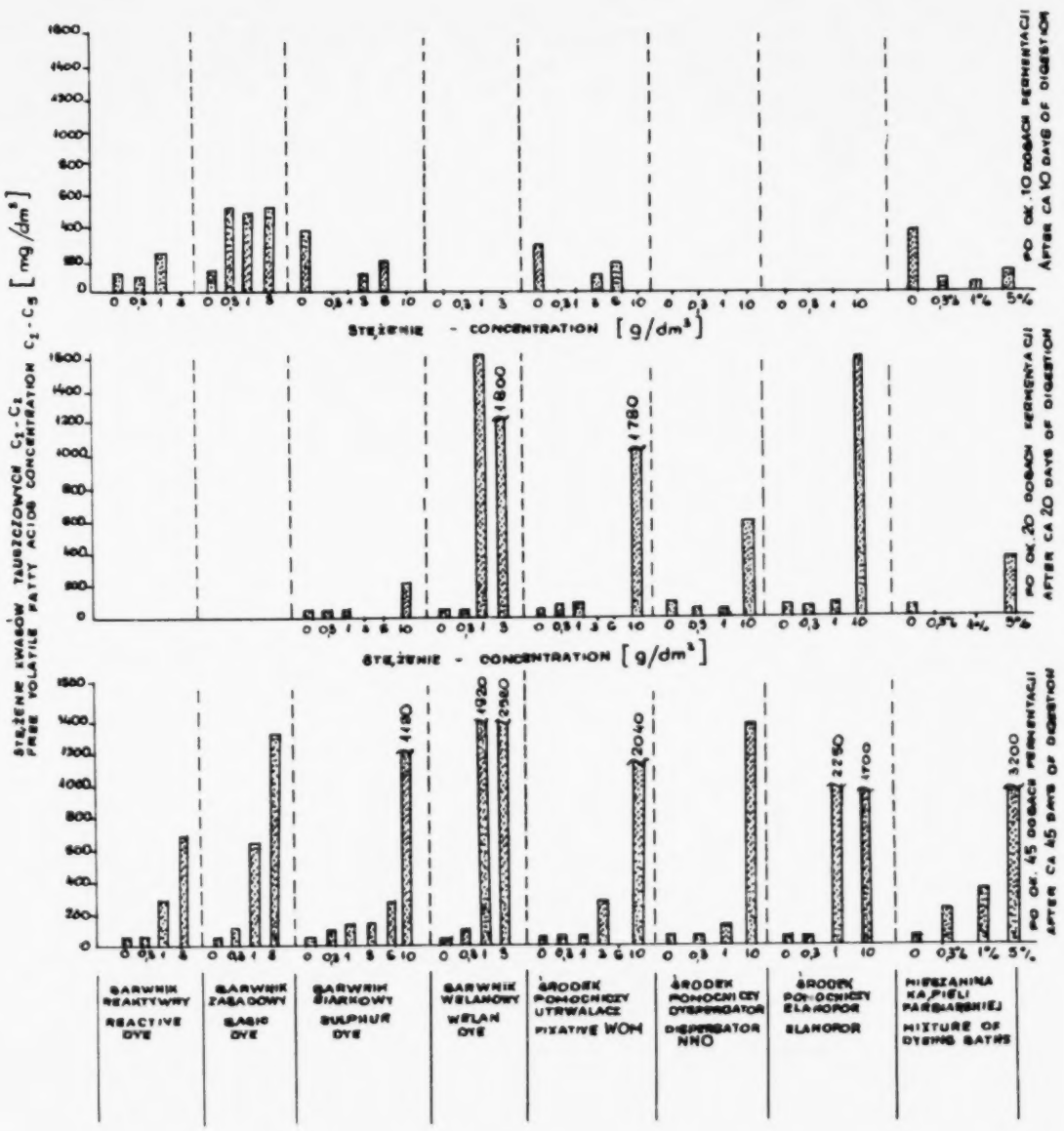
The samples containing an addition of reactivated dispersed dyes indicated an exceptional reduction of 14 percent and 20 percent.

A decreased gas production was observed at the initial period of digestion for some dyes, namely the dispersed, basic and welan dyes. The pH value and alkalinity of the oversludge liquid did not indicate disturbances in the digestion proceeding. The sludge analysis done after 45 days of digestion revealed a loss of volatile parts of about 25 percent to 40 percent. The digestion degree of sludges was about 23 percent to 42 percent, where the lowest degree related to the sludges with the metal complex and welan dyes addition.

The volatile fatty acids content in the oversludge liquid approximated the content in reference samples after 20 days digestion. The 1.0 g/dm^3 concentration of the following dyes: metal complex, active, basic, dispersed and welan, caused considerable disturbances in the digestion process. The gas produced per 1 g of solid mass of sludge after 41 days of digestion decreased significantly and in relation to the reference sample reduced by about 38, 56, 65, 66, and 71 percent for the particular samples. A decrease of volatile parts was observed when the gas production was reduced. In the oversludge liquid samples containing basic and welan dyes, an increase of fatty acids concentration to 620 mg/dm^3 and 1980 mg/dm^3 after 45 days was found. In the case of welan dye, after 20 days of digestion there was an increase of fatty acids to 1630 mg/dm^3, whereas after the same digestion period the concentration in reference sample was of 50 mg/dm^3.

The sludge digestion degree was low, i.e., from 15 percent to 18 percent when for the reference sludges it was about 30 percent. The sludges after digesting were characterized by poor dewatering which was expressed in an increased filter resistant coefficient.

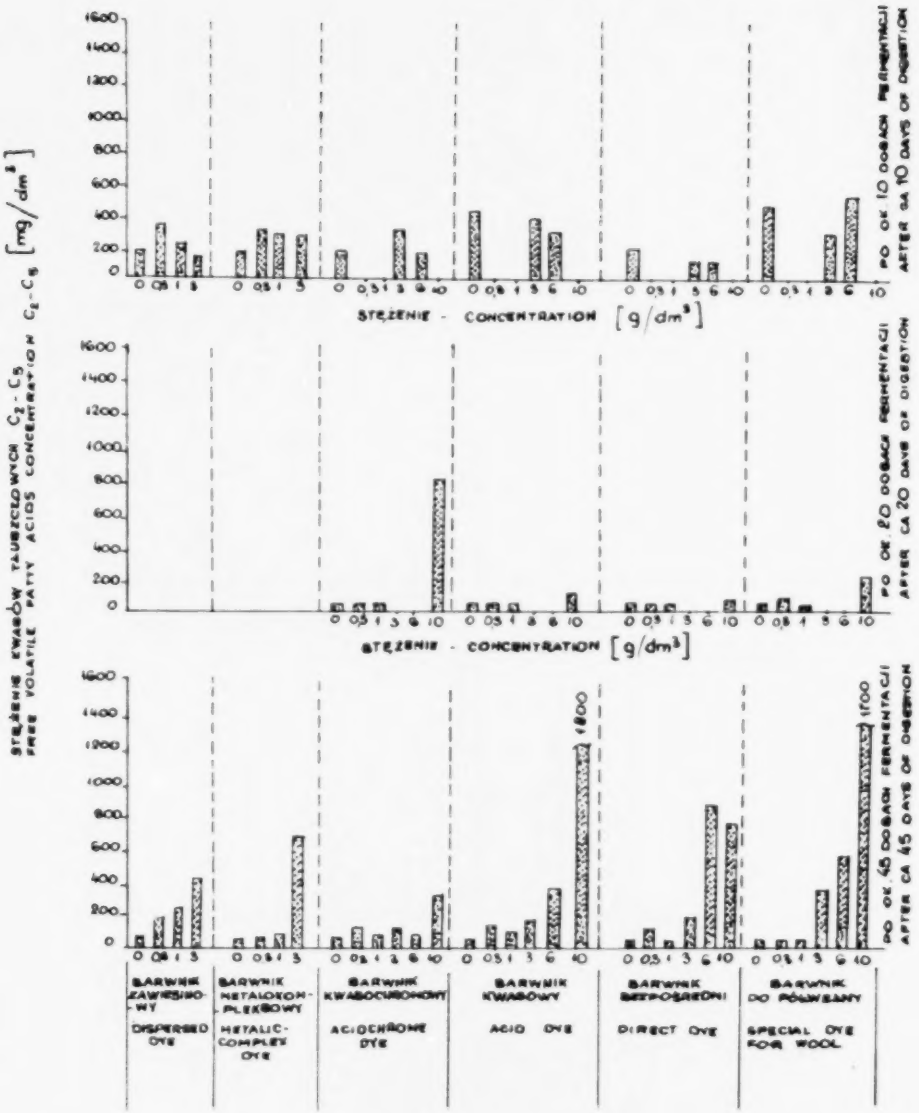
The other dyes, i.e., the chrome dye, the direct dye, the acid dye, the sulfur dye, and the half-wool dye, all of 1.0 g/dm^3 concentration did not inhibit the digestion process. Only in the case of the sulfur dye a decreased gas production in the initial digestion process was found. Significant pH values and alkalinity changes have not been observed in the oversludge liquid, and the content of free volatile fatty acids after 45 days digestion was similar to the reference samples, being of 50 to 100 mg/dm^3.



Rys.77. Stężenie sumaryczne wolnych lotnych kwasów tłuszczowych w procesie beztlenowej fermentacji osadów ściekowych zawierających barwniki i środki pomocnicze.

Figure 77. Summary concentration of free volatile fatty acids in the anaerobic digestion process of sludge containing tested dyes and assistants.

PART I



Rys 77. Stężenie sumaryczne wolnych lotnych kwasów tłuszczowych w procesie beztlenowej fermentacji osadów ściekowych zawierających barwniki i środki pomocnicze.

Figure 77. Summary concentration of free volatile fatty acids in the anaerobic digestion process of sludge containing tested dyes and assistants.

PART II

The gas production after 41 days of digestion referring to the 1 g of sludge solid mass was reduced from 10 percent to 13 percent.

At the 3.0 g/dm^3 content of dyes, an inhibition of sludge digestion process was observed. It relates to the sludges containing the active, basic, dispersed, acid and half-wool dyes. The gas production after 41 days of digestion, referring to the 1 g of sludge solid mass, was respectively reduced as follows: 78, 70, 85, 88, 56, and 53 percent.

A rather low sludge digestion rate, ranging from 6 percent to 13 percent, was noted, except for the sludge with half-wool dye addition for which the digestion degree was of about 22 percent. Generally, an increase in the volatile fatty acids concentrations in the oversludge liquid of samples containing the above mentioned dyes was found during the digestion. The 3.0 g/dm^3 concentration of chrome, sulfur and direct acids did not inhibit the digestion.

The gas production, as well as the quantity of removed volatile parts, were approximately the values obtained for the reference samples.

When these dyes concentration were increased to 6.0 g/dm^3, the reduction of gas production was of 24, 72 and 37 percent.

The maximum concentrations of dyes and assistants existing separately in sludges at which the digestion process was not disturbed, were determined as follows during the studies:

Active dye	0.3 g/dm^3
Dispersed dye	0.3 g/dm^3
Basic dye	0.3 g/dm^3
Metalcomplex dye	0.3 g/dm^3
Welan dye	0.3 g/dm^3
Acid dye	1.0 g/dm^3
Half-wool dye	1.0 g/dm^3
Direct dye	3.0 g/dm^3
Sulfuric dye	3.0 g/dm^3
Chrome dye	6.0 g/dm^3
Elanofor - assistant	0.3 g/dm^3
Fixing agent - assistant	1.0 g/dm^3
Dispersing agent - assistant	1.0 g/dm^3

The higher concentrations of the investigated dyes equal to 10.0 g/dm^3 almost entirely inhibited the sludge digestion process. A significant accumulation of fatty acids was observed in the sludge samples after about 45 days digestion, except the sample containing the direct dye for which the reduction of gas production was 37 percent after 41 days of digestion. In the oversludge liquid of the mentioned sample, the lowest content of fatty acids equaled to 300 mg/dm^3.

From all the tested assistants, the elanofor revealed the most undesirable influence on the digestion process. A concentration of 1.0 g/dm^3 caused an 80 percent reduction of gas production.

The analysis of oversludge liquid, after 45 days digestion, indicated a pH and alkalinity decrease, and a reasonable accumulation of fatty acids. The presence of dispersing agent NNO in sludges in concentrations of 0.3 g/dm^3 and 1.0 g/dm^3 did not inhibit the digestion process, but 10.0 g/dm^3 concentration of it reduced the gas production by 54 percent.

A significant increase in volatile fatty acids concentrations has been observed in the oversludge liquid. An inhibiting effect of the fixing agent WOM on the digesting process occurred at the 3.0 g/dm^3 concentration causing a reduction of gas production by about 70 percent.

The 0.3 percent and 1.0 percent solutions of dyeing bath mixture in sludges did not have an inhibiting effect on the digestion process, as expressed mainly in the quantity of the produced gas.

An adverse influence of 5 percent solution of dyeing bath in sludges on the methane digestion process was noted, however the concentrations of particular sludge mixture components were lower than the concentrations which in the separate samples did not inhibit the digestion process.

Comparing the obtained results for the particular contaminants and for the mixture, it can be concluded that there exists a synergistic effect of components in the multicomponent mixtures. It can be then expected that the dyeing wastewater, even at low concentrations, may inhibit the methane sludge digestion process at an undesirable quality composition.

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